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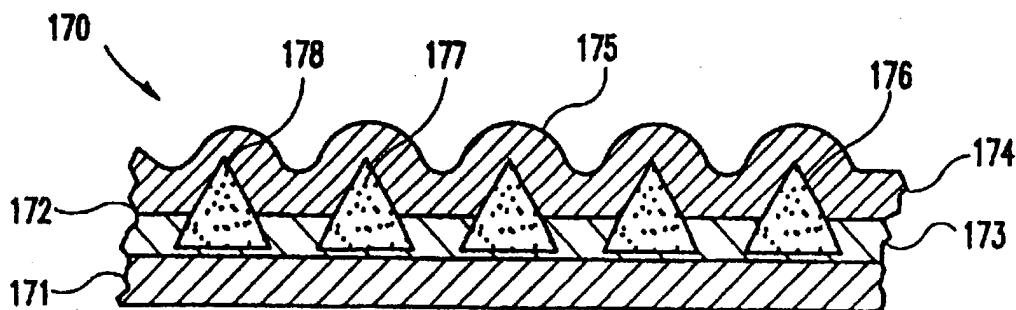
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(54) Title: METHOD OF MODIFYING AN EXPOSED SURFACE OF A SEMICONDUCTOR WAFER



(57) Abstract

A method of modifying an exposed surface of a semiconductor wafer that includes the steps of: (a) contacting the surface with a fixed abrasive article having a three-dimensional textured abrasive surface that includes a plurality of abrasive particles and a binder in the form of a pre-determined pattern; and (b) relatively moving the wafer and the fixed abrasive article to modify said surface of the wafer.

METHOD OF MODIFYING AN EXPOSED SURFACE OF A SEMICONDUCTOR WAFER

Background Of The Invention

5 1. Field of the Invention

This invention relates to modifying an exposed surface of a semiconductor wafer.

2. Description of the Related Art

10 In the course of integrated circuit manufacture, a semiconductor wafer typically undergoes numerous processing steps, including deposition, patterning, and etching steps. Additional details on how semiconductor wafers are manufactured can be found in the article "Abrasive Machining of Silicon" by Tonshoff, H.K.; Scheiden, W.V.; Inasaki, I.; Koning, W.; Spur, G. published in the
15 Annals of the International Institution for Production Engineering Research, Volume 39/2/1990, pages 621 to 635. At each step in the process, it is often desirable to achieve a pre-determined level of surface "planarity," "uniformity," and/or "roughness." It is also desirable to minimize surface defects such as pits and scratches. Such surface irregularities may affect the performance of the final
20 semiconductor device and/or create problems during subsequent processing steps.

One accepted method of reducing surface irregularities is to treat the wafer surface with a slurry containing a plurality of loose abrasive particles dispersed in a liquid and a polishing pad. One problem with such slurries, however, is that the process must be carefully monitored in order to achieve the desired wafer
25 topography. Another problem is that the slurries generate a large number of particles which must be removed and disposed following wafer treatment.

and/or "uniformity" desired will vary depending upon the individual wafer and the application for which it is intended, as well as the nature of any subsequent processing steps to which the wafer may be subjected. In general, however, there are several preferred methods of measuring the degree of "planarity," "roughness," and/or "uniformity."

One preferred method is to measure the Ra value of the wafer surface (which provides a measure of "roughness"). The wafer surface is preferably modified to yield an Ra value of no greater than about 20 Angstroms, more preferably no greater than about 15 Angstroms, and even more preferably no greater than about 10 Angstroms.

The average cut rate depends upon the composition and topography of the particular wafer surface being treated with the abrasive article. In the case of metal oxide-containing surfaces (e.g., silicon dioxide-containing surfaces), average cut rates of at least about 500, 1,000, 1,500, or 2,000 Angstroms/minute may successfully be achieved.

The size of the abrasive particles depends in part upon the particular composition of the abrasive article and any liquid used during the process. In general, however, abrasive articles in which the abrasive particles have an average particle size no greater than about 5 micrometers are preferred. Even more preferred are abrasive articles in which the average abrasive particle size is no greater than 1 micrometer, in particular no greater than about 0.5 micrometer.

To avoid harming the surface of the semiconductor wafer (particularly where the wafer surface is a metal oxide-containing surface such as a silicon dioxide-containing surface), the abrasive particles may have a Mohs hardness value no greater than about 8. Examples of preferred abrasive particles include metal oxide particles such as ceria. The abrasive particles may be used in combination with filler particles. Examples of preferred filler particles include carbonates (e.g., calcium carbonate), silicates (e.g., magnesium silicate, aluminum silicate, calcium silicate, and combinations thereof), and combinations thereof. Plastic filler particles may also be used.

abrasive article features a backing having a surface that includes the abrasive composites in the form of a coating, each of the composites preferably has substantially the same orientation relative to the backing.

5 In a second aspect, the invention features a method of modifying an exposed surface of a semiconductor wafer that includes the steps of:

(a) contacting the surface with a three-dimensional, textured, fixed abrasive article that includes a plurality of precisely shaped abrasive composites and a binder; and

10 (b) relatively moving the wafer and the fixed abrasive article to modify said surface of the wafer.

In a third aspect, the invention features a method of modifying an exposed surface of a semiconductor wafer that includes the steps of:

(a) contacting the surface with a three dimensional, textured, fixed abrasive article that includes a plurality of abrasive particles and a binder that
15 includes a resin and a plasticizer in an amount sufficient to increase the erodibility of the abrasive surface relative to the same abrasive surface in the absence of the plasticizer; and

(b) relatively moving the wafer and the fixed abrasive article to modify the surface of the wafer. The binder preferably includes at least 25% by weight of
20 the plasticizer (more preferably between about 40% and about 75% by weight) based upon the combined weight of the plasticizer and the resin.

In a fourth aspect, the invention features a method of modifying an exposed surface of a semiconductor wafer comprising a metal oxide comprising the steps of:

(a) contacting the surface with a three-dimensional, textured, erodible,
25 fixed abrasive article comprising a plurality of abrasive particles and a binder arranged in the form of a pre-determined pattern; and

(b) relatively moving the wafer and the fixed abrasive article to modify the surface of the wafer.

Other features, advantages, and constructs of the invention will be better understood from the following description of figures and the preferred embodiments of the present invention.

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Brief Description Of The Drawings

Figure 1 is an enlarged schematic cross sectional view of a portion of a semiconductor wafer prior to surface modification;

Figure 2 is an enlarged schematic cross sectional view of a portion of a semiconductor wafer after surface modification;

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Figure 3 is a partial side schematic view of one apparatus for modifying the surface of a semiconductor wafer;

Figure 4 is an enlarged cross sectional view of a portion of a three-dimensional, textured, fixed abrasive article useful in the process of the present invention;

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Figure 5 is an enlarged cross sectional view of a portion of another three-dimensional, textured, fixed abrasive article useful in the process of the present invention;

Figure 6 is a top plan view of a portion of a three-dimensional, textured, fixed abrasive article useful in the process of the present invention;

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Figure 7 is an isometric view of a portion of a three-dimensional, textured, fixed abrasive article useful in the process of the present invention;

Figure 8 is an isometric view with parts shown in cross sectional of a portion of another three-dimensional, textured, fixed abrasive article useful in the process of the present invention;

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Figures 9-12 are enlarged cross sectional views of portions of additional three-dimensional, textured, fixed abrasive articles useful in the process of the present invention;

Figure 13 is an enlarged isometric view of a semiconductor wafer showing reference planes;

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Figure 14 is an enlarged isometric view of a semiconductor wafer showing reference planes;

interconnects 4 and over the front surface 8 of dielectric layer 3. First insulating layer 5 is typically a metal oxide such as silicon dioxide, BPSG (borophosphosilicate glass), PSG (phosphosilicate glass), or combinations thereof. The resulting insulating layer 5 often has a front surface 6 that may not be as "planar" and/or "uniform" as desired.

Before an additional layer of circuitry can be applied via a photolithography process, it is desired to treat surface 6 of the first insulating layer to achieve the desired degree of "planarity" and/or "uniformity;" the particular degree will depend on many factors, including the individual wafer and the application for which it is intended, as well as the nature of any subsequent processing steps to which the wafer may be subjected. For the sake of simplicity, throughout the remainder of this application this process will be referred to as "planarization". Figure 2 illustrates the wafer shown in Figure 1 after planarization (depicted in Figure 2 as semiconductor wafer 20). As a result of planarization, the front surface 22 of insulating layer 5 should be sufficiently planar such that when the subsequent photolithography process is used to create a new circuit design, the critical dimension features can be resolved. These critical dimension features form the circuitry design.

With respect to the wafer shown in Figure 1, planarization occurs on first insulating layer 5; however, other layers may be planarized in the course of the wafer fabrication process. In fact, after each additional layer of insulating material is applied over the metal interconnects, planarization may be needed. In fact, there may be anywhere from one to ten, or even greater than ten layers of circuitry, metal interconnects and metal oxide insulating layers. In addition, the blank wafer may need to be planarized as well.

Semiconductor Wafer Parameters

There are several well-known properties that can be evaluated using art-recognized techniques to determine if the semiconductor wafer has been sufficiently planarized. These properties include flatness (measured in terms of the Total Indicated Runout (TIR)), surface finish (measured in terms of the average

Prior to planarization, the distance between first imaginary plane 262 and lowest point 259 is typically greater than about 0.5 micrometers. In some instances, the distance between first imaginary plane 262 and lowest point 259 (i.e., the TIR) is greater than 0.5 micrometer, sometimes greater than about 0.8 micrometer or even greater than about 1 to 2 micrometers. The actual value of this distance depends in part upon the design and fabrication of the semiconductor wafer.

Figure 14 illustrates the wafer shown in Figure 13 following planarization (and thus is similar to the wafer shown in Figure 2). Planarized semiconductor wafer 277 comprises semiconductor base 251 having front surface 253 and back surface 252. Over front surface 253 of semiconductor base 251 is dielectric layer 254 having front surface 255. Over front surface 255 of dielectric layer 254 there are plurality of metal interconnects 265, 264 and 267. Between these metal interconnects is insulating layer 263. As a result of planarization, outermost surface 275 (which includes high points 276 and low points 278) of semiconductor wafer 277 has become more level and uniform.

The extent of planarization can be envisioned through the use of reference planes shown in Figure 14. There is first reference plane 271 that is formed from back surface 252 of semiconductor base 251. There is second imaginary plane 268 that intersects or touches the outermost portion or highest point 276 of outermost surface 275 of semiconductor wafer 277. Lowest point 278 is the bottommost area on outermost portion 275 of semiconductor wafer 277. As a result of planarization, it is preferred that for a specific region of the wafer, the distance between second imaginary plane 268 and lowest point 278 (i.e., the TIR) over this region is less than about 5000 Angstroms, preferably no more than about 1500 Angstroms. The particular TIR value will depend upon the individual wafer and the application for which it is intended, as well as the nature of any subsequent processing steps to which the wafer may be subjected. In general, prior to planarization, the average TIR of a metal oxide-containing wafer surface is greater than about 2500 Angstroms, usually in the range of about 1.0 to 1.2 micrometers. After planarization, the average TIR is preferably less than about 2500 Angstroms, more preferably less than about 2000 Angstroms, and even more preferably less than

layer in areas between the metal interconnects before and after planarization. The amount removed from each area is determined and the ratio calculated.

The particular value for the planarization ratio will depend upon the individual wafer and the application for which it is intended, as well as the nature of any subsequent processing steps to which the wafer may be subjected. In general, the planarization ratio should be less than 2. Typically, suitable ratios range between about 1.0 to about 2.0, preferably between about 1.0 to about 1.6, more preferably about 1.0 to about 1.4, and most preferably between about 1.0 to about 1.2. A planarization ratio of one is typically preferred because this indicates that there is effectively no dishing.

Defects

Another important parameter to determine if a semiconductor wafer has been sufficiently planarized is the number of defects remaining in the treated wafer surface following planarization. One type of defect is known in the industry as a "pit" or an undesirable depression in the wafer surface. Another defect is known in the industry as a "dig" or "skid," and represents a series of undesirable coarse scratches that are close together.

The number and type of defects can be determined using art-recognized techniques, including laser light scattering. In general, it is desired to minimize the number of defects.

Apparatus

Figure 3 illustrates a very simplified apparatus for planarizing semiconductor wafers useful in the process according to the invention. This type of apparatus and numerous variations and other types of apparatus are well known in the art for use with polishing pads and loose abrasive slurries. An example of a suitable commercially available apparatus is a CMP machine available from IPEC/WESTECH of Phoenix, AZ.

As shown in Figure 3, apparatus 30 comprises head unit 31 that is connected to a motor (not shown). Chuck 32 extends from head unit 31; an

metal oxide surfaces (e.g., silicon dioxide surface), the particulate fillers preferably should have a Mohs hardness less than about six. Examples of suitable fillers for this purpose include materials such as talc, gypsum, calcium carbonate, fluorite apatite and the like. Also suitable in the case of metal oxide-containing surfaces are
5 polymeric filler particles, e.g., particles made from polyester, polycarbonate, polyamide, polyolefin, phenolic resin, and the like.

Examples of suitable thermosetting resins for use in the particulate-filled composite include phenolic resins, epoxy resins, acrylate resins, urea-formaldehyde resins, melamine formaldehyde resins and the like. It is also feasible to impregnate
10 a cloth or a nonwoven substrate with the thermosetting resin and solidify the thermosetting resin to form a substrate impregnated with a solidified thermoset resin. Examples of such cloth include cotton cloth, nylon cloth, and polyester cloth. The substrate may also be a nonwoven substrate such as a paper substrate.

Examples of suitable commercially available wafer holders include those
15 sold under the designations "G-10", "NTA" and "0500-RB" by Rodel.

Referring to Figure 3, wafer holder 33 will typically have a diameter between about 10 to about 500 mm, preferably between about 15 to about 250 mm, more preferably between about 20 to about 300 mm. Wafer holder 33 may contain one or more semiconductor wafers. In some instances there may be between 1 and
20 40 semiconductor wafers per wafer holder.

The speed at which wafer holder 33 rotates will depend on the particular apparatus, planarization conditions, abrasive article, and the desired planarization criteria. In general, however, wafer holder 33 rotates between about 2 to about 1,000 rpm, typically between about 5 to about 500 rpm, preferably between about
25 10 to about 300 rpm and more preferably between about 30 to about 150 rpm. If the wafer holder rotates too slowly or too fast, then the desired cut rate may not be achieved.

Wafer holder 33 may rotate in a circular fashion, spiral fashion, a non-uniform manner, elliptical fashion as a figure eight, corkscrew, or a random
30 motion fashion. The preferred mode is for the wafer holder to rotate in a circular

the resilient element and is at least about 100 MPa. Suitable subpad constructions are disclosed in U.S. Patent Application Serial No. 08/694,357.

The means used to attach the abrasive article to the sub pad preferably holds the abrasive article flat and rigid during planarization. The preferred attachment means is a pressure sensitive adhesive (e.g., in the form of a film or tape). Representative examples of pressure sensitive adhesives suitable for this purpose include those based on latex crepe, rosin, acrylic polymers and copolymers (e.g., polybutylacrylate and other polyacrylate esters), vinyl ethers (e.g., polyvinyl n-butyl ether), alkyd adhesives, rubber adhesives (e.g., natural rubber, synthetic rubber, chlorinated rubber), and mixtures thereof. One preferred pressure sensitive adhesive is an isooctylacrylate:acrylic acid copolymer. The pressure sensitive adhesive is preferably laminated or coated onto the back side of the abrasive article using conventional techniques.

In one preferred embodiment, the abrasive article is a coated abrasive article having of a backing which supports an abrasive coating on one surface, a pressure sensitive adhesive coating on the opposite back surface, wherein the pressure sensitive adhesive coating comprises two layers:

i) a first layer that comprises a pressure sensitive adhesive coating, with the first layer having an inner surface in direct contact with the back surface of the coated abrasive backing and an opposite outer surface, and

ii) a second layer over the outer surface of the first layer, comprising clumps of particles substantially uniformly distributed over and protruding from the first layer, at least the outermost area of these clumps of particles being free of the pressure sensitive adhesive. This type of pressure sensitive adhesive coating is further illustrated in U.S. Patent No. 5,141,790.

In many instances, the abrasive article is in the form of a disc having a diameter typically greater than 25 cm, often greater than 36 cm and sometimes greater than 50 cm in diameter. With these large diameter discs, it is often difficult to accurately place the abrasive disc on the sub pad. This layered pressure sensitive adhesive construction provides a means to allow the disc to "slide" around until the

should be at least 100 Angstroms per minute, preferably at least 500 Angstroms per minute, more preferably at least 1000 Angstroms per minute, and most preferably at least 1500 Angstroms per minute. In some instances, it may be desirable for the cut rate to be as high as at least 2000 Angstroms per minute, and even 3000 or 4000 Angstroms per minute. If the material being removed during planarization is harder and/or more chemically durable than silica, then the cut rates may tend to be lower. Conversely, if the material being removed during planarization is softer than silica, then the cut rates may tend to be higher. However, although it is generally desirable to have a high cut rate, the cut rate must be selected such that it does not compromise the desired topography of the wafer surface.

During planarization, it is generally preferred that the abrasive article provide a consistent cut rate across the entire wafer surface. In addition, it is also generally preferred the abrasive article provide a consistent cut rate between consecutive planarization steps to achieve good process control.

The interface pressure between the abrasive article and semiconductor wafer (i.e., the contact pressure) is preferably less than about 20 psi, more preferably less than about 10 psi, even more preferably less than about 8 psi, and most preferably less than 5 psi and even as low as 3 psi. It has been discovered that the fixed abrasive article used in the method according to the invention can still provide a good cut rate at a low interface pressure. The lower pressure is desired because it improves planarization, minimizes dishing, and permits the use of a lighter weight planarization apparatus. Also, two or more processing conditions within a planarization process may be used. For example, a first processing segment may comprise a higher interface pressure than a second processing segment. Rotation speeds of the wafer and/or the abrasive article also may be varied during the planarization process.

The planarization process is preferably conducted in the presence of a liquid medium, which is chosen based upon the composition of the wafer surface being planarized to provide the desired planarization without adversely affecting or damaging the wafer.

The liquid medium may also include a chemical etchant. Although not wishing to be bound by any theory, it is theorized that the chemical etchant may "attack" and possibly react with the outermost surface of the semiconductor wafer. The abrasive article of the invention then removes the resulting material formed on the outermost surface of the semiconductor wafer. Examples of chemical etchants include strong acids (e.g., sulfuric acid, hydrofluoric acid, and the like) and oxidizing agents (e.g., peroxides).

The liquid medium may also help break down the surface of the fixed abrasive article, thereby increasing the erodibility of the article during planarization. For example, where the abrasive article includes an abrasive coating containing a water-soluble binder or a water-sensitive filler such as wood pulp, a water-containing liquid medium will result in water dissolving or being absorbed into the abrasive coating, thereby enhancing erodibility.

The liquid medium may also contain additives such as surfactants, wetting agents, buffers, rust inhibitors, lubricants, soaps, and the like. These additives are chosen to provide the desired benefit without damaging the underlying semiconductor wafer surface. A lubricant, for example, may be included in the liquid medium for the purpose of reducing friction between the fixed abrasive article and the semiconductor wafer surface during planarization. It may be added to the liquid medium prior to planarization, or may be supplied in the form of a second stream during planarization. Examples of suitable lubricants include metal salts of fatty acids (e.g., zinc stearate, calcium stearate and lithium stearate), graphite, mica, molybdenum disulfide, talc, polyamides, boron nitride, sulfides, waxes, glycol ethers, glycerine, silicone compounds, polyvinyl acetate, polyvinyl alcohols, ethylene oxide polymers (e.g., polymers commercially available under the trade designation "Polyox" from Union Carbide Corp.), combinations thereof and the like.

Inorganic particulates may also be included in the liquid medium. These inorganic particulates may aid in the cut rate. Examples of such inorganic particulates include: silica, zirconia, calcium carbonate, chromia, ceria, cerium salts (e.g., cerium nitrate), garnet, silicates and titanium dioxide. The average particle size of these inorganic particulates should be less than about 1,000 Angstroms.

Nevertheless, there are circumstances under which it may be desirable to condition the surface of the fixed abrasive article following a planarization step to remove "worn abrasive particles" and/or to remove any undesirable debris, and thereby enhance the cutting ability of the fixed abrasive article, as well as the quality of the planarized surface. In such circumstances, the surface of the fixed abrasive article may be conditioned according to well-known, conventional techniques, including contacting the abrasive surface with a diamond conditioning tool, brush, bonded abrasive, coated abrasive, metal rod, water jet, or the like. Other techniques include exposure to a laser or to corona energy (e.g., using a Sherman corona treating unit available from Sherman Treathers, Ltd., United Kingdom).

The conditioning operation can occur while the abrasive article remains on the planarization apparatus. Alternatively, the abrasive article can be removed, conditioned, and then returned to the apparatus. In some instances, the semiconductor wafer may be removed from the wafer holder after planarization and the wafer holder used to condition the abrasive article. A conditioning tool may also be placed over the wafer holder or installed in place of the wafer holder to condition the abrasive article.

The abrasive article may also be conditioned during the planarization process itself, e.g., by fitting the planarization apparatus with a conditioning tool such that when the abrasive article is exposed it will come into contact with the conditioning tool, or by arranging the wafer holder such that it contacts and conditions the abrasive article during planarization such that the wafer holder in essence continually conditions the abrasive article during planarization.

Abrasive Article

A. General Structure

The process of this invention involves modifying the surface of a semiconductor wafer with a three-dimensional, textured fixed abrasive article. The abrasive article is preferably long lasting, e.g., the abrasive article should be able to complete at least two, preferably at least 5, more preferably at least 20 and most preferably at least 30 planarization processes. The abrasive article should preferably

abrasive particles are expelled from the abrasive article, thereby exposing new abrasive particles. The expelled abrasive particles may then become dispersed in the liquid medium, depending on machine type and operating conditions and the choice of abrasive article and its degree of erodibility.

5 The abrasive article also has a "texture" associated with it; i.e., it is a "textured" abrasive article. This can be seen with reference to the abrasive articles illustrated in Figures 4 and 17 and described above, in which the pyramid-shaped composites are the raised portions and in which the valleys between the pyramids are the recessed portions. Although not wishing to be bound by any theory, it is
10 theorized that this texture provides several functions and advantages as follows.

 The first function is that the recesses will act as channels to help distribute the liquid medium over the entire semiconductor wafer surface when carrying out the inventive methods described herein. The second function of the recesses is to also act as channels to help remove the worn abrasive particles and other debris
15 from the semiconductor wafer surface. This also helps to minimize the need to condition the abrasive article between the planarization of two semiconductor wafers.

 The third function is to protect the abrasive article from the phenomenon known in the art as "stiction." If the abrasive coating is smooth rather than
20 textured, then this smooth abrasive coating tends to stick or become lodged against the semiconductor wafer surface. Stiction results in the abrasive article being unable to mechanically planarize the semiconductor wafer. Stiction also inhibits chemical planarization, i.e., inhibits the liquid medium from interacting with the outermost surface of the semiconductor wafer. Due to the discontinuity of the
25 abrasive coating imparted by the recessed portions of the textured surface, stiction is minimized.

 The fourth function is the ability to apply a higher unit pressure on the raised abrasive coating portions, thus helping to expunge expelled abrasive particles from the abrasive surface and expose new abrasive particles.

30 It is also preferred that the abrasive article be erodible, i.e., able to wear away controllably with use. Erodibility is desired because it results in expelled

contact platen. The contact roll or contact platen supports the back side of the abrasive article as it contacts the semiconductor wafer during planarization.

One method of providing a three-dimensional, textured, fixed abrasive article is generally as follows. A slurry containing a mixture of a binder precursor and a plurality of abrasive grains is applied onto a production tool having cavities which are the negative of the desired shape of the textured surface. A backing is brought into contact with the exposed surface of the production tool such that the slurry wets the surface of the backing. Then, the binder can be at least partially solidified, cured, or gelled. The abrasive article is then removed from the production tool and fully cured if it was not fully cured in the previous step. Alternatively, the slurry can be applied onto the surface of the backing and then the production tool can be brought into contact with the slurry on the backing. The abrasive coating thus comprises a plurality of abrasive "composites" on a backing.

Another method of providing a three-dimensional, textured, fixed abrasive article is generally as follows. A backing having a contour generally corresponding to the desired shape of the textured surface is provided. A slurry of abrasive particles in a binder precursor is then coated onto the contoured surface of the backing and cured in such a manner that the cured abrasive coating will have a textured surface corresponding generally to the contour of the backing. In one aspect of this method, an embossed backing is provided to make the abrasive article.

Certain modifications may be made in the three-dimensional, textured, fixed abrasive article to improve or otherwise alter performance. For example, the abrasive article may be perforated to provide openings through the abrasive layer and/or the backing to permit the passage of fluids before, during or after use.

Specific components of the abrasive article will now be described.

1. Backing

The abrasive article may be in the form of a backing provided with an abrasive coating. Preferred backings of abrasive articles for semiconductor wafer planarization are very uniform in thickness. If the backing is not sufficiently

to form the backing. The embossed pattern can be any texture. For example, the pattern can be in the form of an hexagonal array, ridges, lattices, spheres, pyramids, truncated pyramids, cones, cubes, blocks, rods, and the like.

The backing may also contain a treatment to modify its physical properties.

- 5 These treatment coats are well known in the abrasive art and include acrylate-based treatment coats, phenolic treatment coats and phenolic/latex treatment coats.

The backing may also be a foamed backing, e.g., a polymeric foam such as a polyurethane foam.

- 10 A pressure sensitive adhesive can be laminated to the nonabrasive side of the backing. Likewise, a foam substrate can be laminated to the backing.

- In some instances, the back side or back surface of the backing may contain a friction coating. This friction coating may comprise a plurality of friction particles bonded to the backing by means of a friction coating binder. Friction particles may be any suitable material to create the desired coefficient of friction. Examples of
15 suitable friction particles include both inorganic particles and organic particles, e.g., abrasive particles and/or filler particles. Alternatively, the friction coating may comprise a coating such as a urethane coating or a rough organic coating.

2. Abrasive Particles

- 20 The abrasive article comprises abrasive particles and a binder. The abrasive particles may be homogeneously dispersed in the binder or alternatively the abrasive particles may be non-homogeneously dispersed. It is generally preferred that the abrasive particles be homogeneously dispersed so that the resulting abrasive coating provides a more consistent cutting ability.

- 25 For semiconductor wafer planarization, fine abrasive particles are preferred. The average particle size of the abrasive particles can range from about 0.001 to 50 micrometers, typically between 0.01 to 10 micrometers. The particle size of the abrasive particle is typically measured by the longest dimension of the abrasive particle. In almost all cases there will be a range or distribution of particle sizes. In
30 some instances it is preferred that the particle size distribution be tightly controlled

inorganic abrasive particles can further be divided into "hard" inorganic abrasive particles (i.e., those having a Mohs hardness of 8 or greater) and "soft" inorganic abrasive particles (i.e., those having a Mohs hardness less than 8).

5 Examples of suitable abrasive particles include fused aluminum oxide, heat treated aluminum oxide, white fused aluminum oxide, black silicon carbide, green silicon carbide, titanium diboride, boron carbide, silicon nitride, tungsten carbide, titanium carbide, diamond, cubic boron nitride, hexagonal boron nitride, garnet, fused alumina zirconia, alumina-based sol gel derived abrasive particles and the like. The alumina abrasive particle may contain a metal oxide modifier. Examples of
10 alumina-based sol gel derived abrasive particles can be found in U.S. Patent Nos. 4,314,827; 4,623,364; 4,744,802; 4,770,671; and 4,881,951. The diamond and cubic boron nitride abrasive particles may be monocrystalline or polycrystalline.

Other examples of suitable inorganic abrasive particles include silica, iron oxide, chromia, ceria, zirconia, titania, tin oxide, gamma alumina, and the like. For
15 planarization of metal oxide-containing wafer surfaces (e.g., silicon dioxide-containing surfaces), it is preferred that the abrasive particles have a Mohs hardness less than 8. Such particles, when properly incorporated into an abrasive article, provide the desired rate of cut and the desired surface finish on the wafer during planarization. Some harder abrasive particles may impart an undesirably
20 coarse surface finish on the oxide-containing wafer surface, so care should be exercised in selection of the appropriate abrasive material, such being within the ability of one skilled in the art.

In the case of metal oxide-containing wafer surfaces (e.g., silicon dioxide-containing surfaces), ceria abrasive particles are useful. Ceria abrasive
25 particles may be purchased from Rhone Poulenc, Shelton, CT; Transelco, New York; Fujimi, Japan; Molycorp, Fairfield, NJ; American Rar Ox, Chaveton City, MA; and Nanophase, Burr Ridge, IL.

The ceria abrasive particles may be essentially free of modifiers or dopants (e.g., other metal oxides). Alternatively, the ceria abrasive particles may contain
30 modifiers and/or dopants (e.g., other metal oxides). In some instances, these metal oxides may react with ceria. It is also feasible to use ceria with a combination of

minimize the agglomeration of the abrasive particles during the manufacture of the abrasive article.

The abrasive particles may be treated with a surface treatment in an amount up to about 25% by weight based solely upon the abrasive particle weight. The
5 abrasive particles are treated with a surface treatment, this amount ranges from about 0.5 to 10% by weight based solely upon the abrasive particle weight.

Examples of suitable surface modification additives include wetting agents (also sometimes referred to as surfactants) and coupling agents. A coupling agent can provide an association bridge between the binder and the abrasive particles.

10 The coupling agent may also provide an association bridge between the binder and the filler particles (to the extent present). Examples of suitable coupling agents include silanes, titanates, and zircoaluminates. Examples of commercially available coupling agents include "A174" and "A1230" from OSI. An example of a commercial dispersant is isopropyl triisosteroyl titanate commercially available from
15 Kenrich Petrochemicals under the trade designation "KR-TTS".

There are various means to incorporate the coupling agent into a slurry to make the abrasive article. For example, the coupling agent may be added directly to the binder precursor. The abrasive particle may contain from about 0 to 30%, preferably between 0.1 to 25%, by weight coupling agent. In yet another mode, the
20 coupling agent may be applied to the surface of the abrasive particles prior to being incorporated into the abrasive article. The abrasive particle may contain up to about 3% by weight coupling agent, based upon the total weight of the abrasive particle and the coupling agent.

It is also feasible to treat the abrasive particles with more than one coupling
25 agent or use a first coupling agent for the abrasive particles and a second different, coupling agent for the filler particles (described below).

If ceria is utilized as the abrasive particle, the ceria may be treated with a coupling agent prior to being added into the binder precursor. An example of such a coupling agent is isopropyl triisosteroyl titanate.

30 Surfactants may also be used as an additive. Examples of surfactants include metal alkoxides, polyalkylene oxides, salts of long chain fatty acids and the

Filler particles generally have an average particle size range between 0.1 to 50 micrometers, typically between 1 to 30 micrometers. In addition, the filler typically has a Mohs hardness less than 5, more preferably less than 4, and most preferably less than about 3, although fillers outside of this hardness range may also be useful. Examples of useful fillers for this invention include: metal carbonates (such as calcium carbonate (chalk, calcite, marl, travertine, marble and limestone)), calcium magnesium carbonate, sodium carbonate, magnesium carbonate), silica (such as quartz, glass beads, glass bubbles and glass fibers) silicates (such as talc, clays such as (montmorillonite), feldspar, mica, calcium silicate, calcium metasilicate, sodium aluminosilicate, sodium silicate) metal sulfates (such as calcium sulfate, barium sulfate, sodium sulfate, aluminum sodium sulfate, aluminum sulfate), gypsum, vermiculite, wood flour, aluminum trihydrate, carbon black, certain metal oxides (such as calcium oxide (lime)), alumina, tin oxide (e.g., stannic oxide), titanium dioxide, metal sulfites (such as calcium sulfite), thermoplastic particles (e.g., polycarbonate, polyetherimide, polyester, polyethylene, polysulfone, polystyrene, acrylonitrile-butadiene-styrene block copolymer, polypropylene, acetal polymers, polyurethanes, nylon particles) and thermosetting particles (such as phenolic bubbles, phenolic beads, polyurethane foam particles, phenolic resins, aminoplast resins, urethane resins, epoxy resins, melamine-formaldehyde, acrylate resins, acrylated isocyanurate resins, urea-formaldehyde resins, isocyanurate resins, acrylated urethane resins, acrylated epoxy resins, and the like). The filler may also be a salt such as a halide salt. Examples of halide salts include sodium chloride, potassium cryolite, sodium cryolite, ammonium cryolite, potassium tetrafluoroborate, sodium tetrafluoroborate, silicon fluorides, potassium chloride, magnesium chloride. Examples of metal fillers include tin, lead, bismuth, cobalt, antimony, cadmium, iron, titanium. Other miscellaneous fillers include sulfur, organic sulfur compounds, graphite, boron nitride, and metallic sulfides. The above mentioned examples of fillers are meant to be a representative showing of some useful fillers, and are not meant to encompass all useful fillers.

One useful filler is calcium carbonate. Other useful fillers include silicates such as magnesium silicate, aluminum silicate, and calcium silicate. The average

4. Binders

Organic Resin

The binders for the abrasive articles of this invention are preferably formed from an organic binder precursor. The binder precursor has a phase that is capable of flowing sufficiently so as to be coatable, and then solidifying. The solidification can be achieved by curing (e.g., polymerizing and/or crosslinking) and/or by drying (e.g., driving off a liquid), or simply upon cooling. The precursor can be an organic solvent-borne, water-borne, or 100% solids (i.e., a substantially solvent-free) composition. Both thermoplastic and thermosetting materials, as well as combinations thereof, can be used as the binder precursor.

In many instances, the abrasive coating is formed from a slurry that comprises a mixture of abrasive particles and a binder precursor. The abrasive coating can comprise by weight between about 1 part abrasive particles to 90 parts abrasive particles and 10 parts binder to 99 parts binder. Preferably the abrasive coating comprises about 30 to 85 parts abrasive particles and about 15 to 70 parts binder. More preferably the abrasive coating comprises about 40 to 70 parts abrasive particles and about 30 to 60 parts binder precursor.

The binder precursor is preferably a curable organic material (i.e., a material capable of polymerizing and/or crosslinking upon exposure to heat and/or other sources of energy, such as E-beam, ultraviolet, visible, etc., or with time upon the addition of a chemical catalyst, moisture, and the like). Binder precursor examples include amino resins (e.g., aminoplast resins) such as alkylated urea-formaldehyde resins, melamine-formaldehyde resins, and alkylated benzoguanamine-formaldehyde resin, acrylate resins (including acrylates and methacrylates) such as vinyl acrylates, acrylated epoxies, acrylated urethanes, acrylated polyesters, acrylated acrylics, acrylated polyethers, vinyl ethers, acrylated oils, and acrylated silicones, alkyd resins such as urethane alkyd resins, polyester resins, reactive urethane resins, phenolic resins such as resole and novolac resins, phenolic/latex resins, epoxy resins such as bisphenol epoxy resins, isocyanates, isocyanurates, polysiloxane resins (including alkylalkoxysilane resins), reactive vinyl resins, and the like. The resins may be in the form of monomers, oligomers, polymers, or combinations thereof.

siloxane groups, nitro groups and phosphate groups. Examples of preferred epoxy resins include 2,2-bis(4-(2,3-epoxypropoxy)-phenyl)propane (diglycidyl ether of bisphenol A) and materials commercially available under the trade designation "Epon 828", "Epon 1004" and "Epon 1001F" from Shell Chemical Co.; and
5 "DER-331", "DER-332" and "DER-334" from Dow Chemical Co. Other suitable epoxy resins include glycidyl ethers of phenol formaldehyde novolac (e.g., "DEN-431" and "DEN-428" available from Dow Chemical Co.)

Examples of ethylenically unsaturated binder precursors include aminoplast monomers or oligomers having pendant alpha, beta unsaturated carbonyl groups,
10 ethylenically unsaturated monomers or oligomers, acrylated isocyanurate monomers, acrylated urethane oligomers, acrylated epoxy monomers or oligomers, ethylenically unsaturated monomers or diluents, acrylate dispersions, and mixtures thereof.

The aminoplast binder precursors have at least one pendant alpha, beta-unsaturated carbonyl group per molecule or oligomer. These materials are
15 further described in U.S. Patent Nos. 4,903,440 and 5,236,472.

The ethylenically unsaturated monomers or oligomers may be monofunctional, difunctional, trifunctional, tetrafunctional or even higher functionality, and include both acrylate and methacrylate-based monomers.
20 Ethylenically unsaturated binder precursors include both monomeric and polymeric compounds that contain atoms of carbon, hydrogen and oxygen, and optionally, nitrogen and the halogens. Oxygen or nitrogen atoms or both are generally present in ether, ester, urethane, amide, and urea groups. Suitable ethylenically unsaturated compounds preferably have a molecular weight of less than about 4,000 and are
25 preferably esters made from the reaction of compounds containing aliphatic monohydroxy groups or aliphatic polyhydroxy groups and unsaturated carboxylic acids, such as acrylic acid, methacrylic acid, itaconic acid, crotonic acid, isocrotonic acid, maleic acid, and the like. Representative examples of ethylenically unsaturated monomers include methyl methacrylate, ethyl methacrylate, styrene, divinylbenzene,
30 hydroxy ethyl acrylate, hydroxy ethyl methacrylate, hydroxy propyl acrylate, hydroxy propyl methacrylate, hydroxy butyl acrylate, hydroxy butyl methacrylate,

urethane diacrylate of 1200 molecular weight diluted with 1,6-hexanediol diacrylate), "EBECRYL 4827" (aromatic urethane diacrylate of 1600 molecular weight), "EBECRYL 4830" (aliphatic urethane diacrylate of 1200 molecular weight diluted with tetraethylene glycol diacrylate), "EBECRYL 6602" (trifunctional aromatic urethane acrylate of 1300 molecular weight diluted with trimethylolpropane ethoxy triacrylate), and "EBECRYL 840" (aliphatic urethane diacrylate of 1000 molecular weight) from UCB Radcure Specialties; and "SARTOMER" resins (e.g., SARTOMER 9635, 9645, 9655, 963-B80, 966-A80, etc.) from Sartomer Co., Exton, PA.

Acrylated epoxies are diacrylate esters of epoxy resins, such as the diacrylate esters of bisphenol A epoxy resin. Examples of commercially available acrylated epoxies include those under the tradename "CMD 3500", "CMD 3600", and "CMD 3700", available from UCB Radcure Specialties.

The binder precursor may also comprise an acrylated polyester resin.

Acrylated polyesters are the reaction products of acrylic acid with a dibasic acid/aliphatic diol-based polyester. Examples of commercially available acrylated polyesters include those known by the trade designations "PHOTOMER 5007" (hexafunctional acrylate of 2000 molecular weight), and "PHOTOMER 5018" (tetrafunctional tetracrylate of 1000 molecular weight) from Henkel Corp.; and "EBECRYL 80" (tetrafunctional modified polyester acrylate of 1000 molecular weight), "EBECRYL 450" (fatty acid modified polyester hexaacrylate) and "EBECRYL 830" (hexafunctional polyester acrylate of 1500 molecular weight) from UCB Radcure Specialties.

Examples of ethylenically unsaturated diluents or monomers can be found in U.S. Patent No. 5,236,472 and U.S. Patent Application Ser. No. 08/474,289. In some instances these ethylenically unsaturated diluents are useful because they tend to be compatible with water. Additional reactive diluents are disclosed in U.S. Patent No. 5,178,646.

The binder precursor can also comprise an acrylate-based dispersion. The acrylate-based dispersion comprises a multitude of acrylate-based droplets suspended in water with the aid of a dispersing agent. Each acrylate-based droplet

problem is to condition the new abrasive article before it is used to planarize a semiconductor wafer, although conditioning is not always preferred because conditioning requires an additional step. It is preferred to formulate the slurry such that this binder film is minimized. Although not wishing to be bound by any theory, one approach to minimize the binder migration during curing is to have a high volume concentration of abrasive particles and/or filler in the binder. This high volume concentration is based upon a packing of the abrasive particles and/or filler in the binder such that there is minimal porosity of abrasive particles and/or filler alone, i.e., without the binder present. This high volume concentration will tend to minimize the pathway(s) for the binder to migrate during curing. One means to achieve this high packing density of the abrasive particles and/or fillers is to use a broad particle size distribution of the abrasive particles and/or filler. In a broad particle size distribution, the smaller particles will tend to fill in between the larger particle sizes. However, the larger particles should not generate undesirable coarse scratches on the semiconductor wafer surface.

Although not wishing to be bound by any theory, another approach to minimize the binder migration during curing is to use a binder precursor that is partially polymerized before it is incorporated into the slurry. The partially polymerized binder precursor will tend to have less mobility and therefore it should migrate less during complete polymerization or curing of the binder precursor. One such binder precursor that can be partially polymerized is an acrylate monomer. However, the binder precursor should not be polymerized to such a degree that when incorporated into a slurry, the resulting viscosity of the slurry is excessively high.

An example of an acrylate monomer that can be partially polymerized is isooctyl acrylate. A combination of a partially polymerized ethylenically unsaturated monomer with another ethylenically unsaturated monomer and/or a condensation curable binder can also be used. Additional details concerning partially polymerized ethylenically unsaturated monomers can be found in U.S. Patent No. 5,256,170.

degree of erodibility. For example, the amount of plasticizer should not be so high that the resulting abrasive article is too erodible. Additionally, sometimes if there is too much plasticizer, there may be poor adhesion between the primer associated with the polyester film backing and the abrasive coating in abrasive articles featuring such a construction.

Although not wishing to be bound by any theory at this time, it is theorized that water-soluble or water-swellaible plasticizers may at least partially leach out of the abrasive coating during semiconductor wafer planarization. When this occurs, it is postulated that it increases the overall erodibility of the abrasive coating. Thus in some instances, it is preferred to utilize water-soluble or water-swellaible plasticizers.

Initiator

In the case of binder precursors containing ethylenically unsaturated monomers and oligomers, polymerization initiators may be used. Examples include organic peroxides, azo compounds, quinones, nitroso compounds, acyl halides, hydrazones, mercapto compounds, pyrylium compounds, imidazoles, chlorotriazines, benzoin, benzoin alkyl ethers, diketones, phenones, and mixtures thereof. Examples of suitable commercially available, ultraviolet-activated photoinitiators have tradenames such as "Irgacure 651" and "Irgacure 184" commercially available from the Ciba Geigy Company and "DAROCUR 1173" commercially available from Merck. Examples of suitable visible light-activated initiators can be found in U.S. Patent No. 4,735,632. Another visible light-activated photoinitiator has the trade name "IRGACURE 369", commercially available from Ciba Geigy Company.

In the case of photopolymerizations, the initiator system may include a photosensitizer as well. Examples include compounds having carbonyl groups or tertiary amino groups and mixtures thereof. Among the preferred compounds having carbonyl groups are benzophenone, acetophenone, benzil, benzaldehyde, o-chlorobenzaldehyde, xanthone, thioxanthone, 9,10-anthraquinone, and other aromatic ketones which can act as photosensitizers. Among the preferred tertiary

Dual-cure and hybrid-cure systems may also be used. In dual-cure systems, curing occurs in two separate stages, via either the same or different reaction mechanisms. In hybrid-cure systems, two curing mechanisms occur at the same time upon exposure to ultraviolet/visible or E-beam radiation.

5

Other Additives

The slurry can further comprise additives such as abrasive particle surface modification additives, coupling agents, fillers, expanding agents, fibers, antistatic agents, initiators, suspending agents, lubricants, wetting agents, surfactants, pigments, dyes, UV stabilizers, complexing agents, chain transfer agents, accelerators, catalysts, and activators. The amounts of these materials are selected to provide the properties desired.

Expanding agents may be included to increase the erodibility of the abrasive article. The expanding agent can be any material that increases the volume of the abrasive coating. It is preferred that when an expanding agent is employed, the average particle size of the abrasive particles is less than 30 micrometers.

Examples of suitable expanding agents include steam, swelling solvents, nitrogen gas, carbon dioxide gas, air as a gas, pentane, hexane, heptane, butene, CFCl_3 , $\text{C}_2\text{F}_3\text{Cl}_3$, vermiculite, toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, hexamethylene diisocyanate, or polyurethane prepolymer which reacted with water to generate carbon dioxide gas. Other suitable expanding agents include a decomposition-type expanding agent such as ammonium carbonate, ammonium bicarbonate, sodium bicarbonate, dinitropentamethylenetetramine, azodicarbonamide, azobisisobutyronitrile, hydrazine compounds such as maleic acid hydrazide, oxalic acid hydrazide, benzenesulfonyl hydrazide, toluenesulfonyl hydrazide, p,p'-hydroxy bis(benzene-sulfonyl hydrazide), and t-alkylhydrazonium salt. Two or more expanding agents may be used in combination with each other.

An example of an expanding agent is an expanding bead commercially available from the Kema Nobel Company, Sundsvall, Sweden under the trade designation "Expancel 551".

Ceramer Binders

Another suitable type of binder is a ceramer binder. "Ceramer" is a term used to identify a curable material containing at least one component that is 1) a precursor of a ceramic or a ceramic particle (i.e., metal oxide particle) and 2) at least one component that is a binder precursor (i.e., precursor of a polymer). The cured ceramer is formed from a ceramer binder precursor comprising: 1) a dispersing liquid, 2) a binder precursor and 3) non-aggregated colloidal metal oxide particles dispersed in the dispersing liquid and the binder precursor. The dispersing liquid can be water (including tap water, distilled water and deionized water) or an organic solvent (including aqueous alcohol solutions, lower aliphatic alcohols, toluene, ethylene glycol, dimethyl acetamide, formamide, and combinations thereof). The preferred dispersing liquid is water, preferably distilled or deionized water. It is preferred that the amount of water in the dispersing liquid is at least 10% by weight, preferably at least 12% by weight and more preferably at least 15% by weight of the total dispersing liquid (i.e., includes the water, binder precursor and not the colloidal metal oxide particles). The preferred binder precursors include ethylenically unsaturated monomers, ethylenically unsaturated oligomers, epoxy resins and combinations thereof.

Suitable colloidal metal oxide particles are non-aggregated metal oxide particles dispersed in a liquid medium to form a sol. These metal oxide particles have an average particle diameter of from about 5 to about 1000 nanometers, preferably from about 10 to about 100 nanometers, and more preferably from about 10 to about 50 nanometers. In some instances these small metal oxide particles will tend to agglomerate due to interparticle attraction. Thus, these metal oxide agglomerates will be greater in particle size than the individual metal oxide particles. These metal oxide particle size ranges are preferred on the basis of both ease of dispersing the metal oxide particles in the binder precursor and the surface finish that will be generated by the abrasive article derived therefrom.

The metal oxide sol particles may be formed of any metal oxide, in any oxidation state. Examples of preferred metal oxides include silica, alumina, zirconia, chromia, antimony pentoxide, vanadia, ceria, titania, with silica being most

Among the ceramers, those having non-aggregated metal oxide particles functionalized with coupling agents have processing advantages over ceramers having non-aggregated metal oxide particles not functionalized with coupling agents. These coupling agents can be organosilanes (e.g., 3-methacryloxyalkyl trimethoxysilane, methacryloxyalkyl trimethoxysilane, phenyl trichlorosilane, phenyltrimethoxysilane, phenyl triethoxysilane, vinyltrimethoxysilane, vinyl triethoxysilane, methyltrimethoxysilane, methyl triethoxysilane, propyltrimethoxysilane, propyl triethoxysilane, octyltriethoxysilane and mixtures thereof), titanates (e.g., isopropyl trisosteroyl titanate), zircoaluminates and combinations thereof. The ceramers having colloidal metal oxide particles functionalized with coupling agents tend to have a lower viscosity than those not functionalized with coupling agents. This reduction in viscosity can then allow the ceramer binder precursor to be filled with more abrasive particles than those ceramers having non-functionalized colloidal metal oxide particles and still provide coatable or processable mixtures. The degree of functionalization of the colloidal metal oxide particles required to allow mixtures comprising ceramer and abrasive particles to remain coatable depends to a large extent on the concentration of colloidal metal oxide particles, the nature of the binder precursor, and the type of coupling agent. If not enough coupling agent is added, the metal oxide particles in the ceramer may not be properly dispersed, which tends to lead to a higher viscosity of the overall ceramer. Conversely, if too much coupling agent is added, this can lead to an overall increase in cost and/or the ceramer may gel. Likewise, if the coupling agent is trifunctional, too much of a trifunctional coupling agent may result in premature gellation of the ceramer.

The coupling agent should be compatible with the chemistry of the binder precursor. If the coupling agent is not compatible with the binder precursor, there may be phase separation or, alternatively, the ceramer may gel. Sometimes this gellation occurs immediately after the ceramer is made and other times this gellation occurs within hours after the ceramer is made. It is preferred that the ceramer have a stable viscosity over a period of at least 24 hours.

acrylate, hydroxy ethyl methacrylate, hydroxy propyl acrylate, hydroxy propyl methacrylate, hydroxy butyl acrylate, hydroxy butyl methacrylate, acrylamide, N,N-dimethyl acrylamide and the like.

5 In general, the concentration of colloidal metal oxide particles in the ceramer can be as high as 70% by weight, with the preferred concentration ranging from about 15% to about 60% by weight. The coupling agent may range anywhere from about 1 to 10% by weight of the metal oxide particles, preferably between 1 to 5% by weight of the metal oxide particles.

10 After the ceramer is made, the abrasive particles are added or dispersed into the ceramer sol to form a slurry. There may be an additional coupling agent added to the ceramer to improve the dispersability of the abrasive particles in the ceramer sol. Alternatively, the abrasive particles may have been pretreated with another coupling agent. The coupling agent for the metal oxide particles in the ceramer binder precursor may be the same or it may be different from the coupling agent for
15 the abrasive particles. Likewise after the ceramer binder precursor is made, an initiator may be added along with the abrasive particles. The initiator can help to accelerate the polymerization of the binder precursor to form the binder.

20 In some instances, the ceramer binder precursor may contain excess water, i.e., for some reason there is excess water which can be undesirable either from a processing and/or a product performance viewpoint. If there is excess water, the water may be removed by any conventional technique. These techniques include vacuum stripping, distillation and the like, with vacuum stripping being preferred. It is preferred that the water be removed to the desired level prior to the addition of the abrasive particles. If too much water is removed from the ceramer binder precursor, it may be difficult to add more water to the ceramer binder precursor.
25

One example of a useful slurry comprises by weight about 1 to about 50 parts colloidal metal oxide particles, (preferably silica particles), about 2 to about 60 parts ethylenically unsaturated binder precursor, 0.1 to 50 parts coupling agent and about 0.1 to about 50 parts water. In another example the ceramer binder precursor comprises by weight about 3 to about 50 parts colloidal metal oxide
30 particles, (preferably silica particles), about 5 to about 35 parts ethylenically

One preferred abrasive article features a plurality of abrasive composites (as defined in the Summary of the Invention, above). These abrasive composites can be precisely shaped (as defined in the Summary of the Invention, above) or irregularly shaped, with precisely shaped composites being preferred. Such a precise shape can be formed, for example, by curing the binder precursor in the slurry while the slurry is both being formed on a backing and filling a cavity on the surface of a production tool, as described in greater detail, below.

The abrasive composite shape can be any shape. Typically the surface area of the base side of the shape that is in contact with the backing is larger in value than that of the distal end of the composite spaced from the backing. The shape of the composite can be selected from among a number of geometric shapes such as a cubic, cylindrical, prismatic, rectangular, pyramidal, truncated pyramidal, conical, truncated conical, cross, and post-like with a top surface which is flat. Another shape is hemispherical as described in PCT WO 95/224,436. The resulting abrasive article can have a mixture of different abrasive composite shapes. The abrasive composites may be arranged in rows, spiral, helix, corkscrew, or lattice fashion, or may be randomly placed.

The sides forming the abrasive composites may be perpendicular relative to the backing or they can be tapered with diminishing width toward the distal end. If the sides are tapered, it is easier to remove the abrasive composite from the cavities of the production tool. The angle forming the taper can range from about 1 to 75 degrees, preferably from about 2 to 50 degrees, more preferably from about 3 to 35 degrees and most preferably between about 5 to 15 degrees. The lower angles tend to be preferred because this tends to result in a more uniform cross sectional area along the height of the abrasive composite. Thus, in general, the taper angle is a compromise between an angle large enough to remove the abrasive composite from the production tool and small enough to create a uniform cross sectional area. The constant cross sectional area is preferred because this provides a more consistent abrasive coating surface area during planarization. This in turn leads to a more consistent cut rate, flatness and surface finish. One preferred shape is a cylinder having a taper angle between 10 to 15 degrees.

In any of the abrasive articles described herein, all of the abrasive composites may have essentially the same shape and size, but the orientation of individual abrasive composites may be different from one another relative to a reference point. If the abrasive article contains a backing, then the reference point may be a plane that is tangent to a point on the side of the backing. One potential advantage of rotating the abrasive composite relative to an adjacent abrasive composite is to increase the packing density of abrasive composites that have a certain shape. In some embodiments, an adjacent abrasive composite is rotated between 5 to 355 degrees, relative to its nearest neighbor. In those embodiments in which adjacent composites are rotated relative to one another, an adjacent abrasive composite is typically rotated between 30 to 120 degrees. In one embodiment, adjacent abrasive composites are rotated about 45 degrees from one another. In another embodiment, the adjacent abrasive composites are mirror images of each other.

It is also possible for all of the abrasive composites to be identically shaped and oriented. Constructions are also possible in which the composites have different shapes and different orientations.

The base of the abrasive composites can abut one another or alternatively, the bases of adjacent abrasive composites may be separated from one another by some specified distance. In some embodiments, the physical contact between adjacent abrasive composites involves no more than 33% of the vertical height dimension of each contacting composite. More preferably, the amount of physical contact between the abutting composites is in the range of 1 to 25% of the vertical height of each contacting composite. It is to be understood that this definition of abutting also covers an arrangement where adjacent composites share a common abrasive material land or bridge-like structure which contacts and extends between facing sidewalls of the composites. Preferably, the land structure has a height of no greater than 33% of the vertical height dimension of each adjacent composite. The abrasive material land is formed from the same slurry used to form the abrasive composites. The composites are "adjacent" in the sense that no intervening

will correspond to the pattern of the cavities on the production tool. The pattern is thus reproducible from article to article.

In one version of the predetermined pattern, the abrasive composites can be in an array or arrangement, by which is meant that the composites are in a regular array such as aligned rows and columns, or alternating offset rows and columns. In some instances, the one row of abrasive composites can be directly aligned in front of a second row of abrasive composites. Alternatively, one row of abrasive composites can be offset from the second row of abrasive composites. It is preferred that adjacent rows of abrasive composites are offset from one another.

Alternatively, the composites can be deployed in a "random" array or configuration. By this it is meant that the composites are not in a regular array of rows and columns as described above. For example, the abrasive composites may be arranged in a manner as described in PCT WO 95/07797 and PCT WO 95/22436. It is understood, however, that this "random" array is a predetermined pattern in that the location of the composites on the abrasive article is predetermined and corresponds to the location of the cavities in the production tool used to make the abrasive article.

The three-dimensional, textured, fixed abrasive article also may have a variable abrasive coating composition. For example, the center of a fixed abrasive disc may contain an abrasive coating that is different (e.g., "softer, harder, or more or less erodible) from the outer region of the abrasive disc.

Particular configurations are shown in Figures 4-12.

Referring to Figure 4, abrasive article 50 comprises backing 59 having front surface 58 in which abrasive coating 57 is bonded on front surface 58 of backing 59. Abrasive coating 57 is three-dimensional and comprises a plurality of abrasive composites 54. In this particular embodiment, abrasive composites 54 are pyramids. There are recesses or valleys 53 between adjacent abrasive composites. There is also more than one row of pyramidal abrasive composites shown in which the second row of abrasive composites is offset from the first row. Abrasive composites 54 comprise a plurality of abrasive particles 56 dispersed in binder 55.

composite. Valley 309 may consist of no abrasive composite and in this case, the backing is exposed.

Another preferred arrangement of abrasive composites is similar to Figure 6, except that each alternating row comprises either abrasive composites having the "cross" shape or abrasive composites having the "x" shape. In this arrangement, the abrasive composites from the odd rows are still offset from the abrasive composites from the even rows.

In the above described arrangements of cross-shaped or "x"-shaped composites, it is preferred that the length of one line forming either the cross or the x shape is about 750 micrometers and the width of one line forming either the cross or the x shape is about 50 micrometers. There is approximately 1270 micrometers distance between the center of one cross to the center of the adjacent x-shaped abrasive composite.

Referring to Figure 7, abrasive article 75 comprises backing 76 having front surface 77 and back surface 78. Abrasive coating 79 consists of series of abrasive composites 80; the binder and abrasive particles are omitted for the sake of simplicity. Abrasive composites 80 have a ridge shape. Ridges 80 are separated by valleys 73. Ridges 80 have upper section 72 that contact the semiconductor wafer during planarization. These ridges are typically continuous and can have any cross sectional shape.

In another embodiment, the ridges of the abrasive composites are non-parallel and non-perpendicular relative to the sides forming the abrasive backing. This type of arrangement is further described in U.S. Patent No. 5,489,235.

Referring to Figure 12, abrasive article 230 comprises backing 231 having pressure sensitive adhesive coating 238 and a protective liner 237. Over front surface 232 of backing 231 is abrasive coating 240. Abrasive coating 240 is three-dimensional and comprises a plurality of abrasive composites 234. There are openings or valleys 241 between adjacent abrasive composites. In this particular example, abrasive composites 234 are truncated pyramids. Abrasive composites 241 comprise a plurality of abrasive particles 235 and binder 236.

compounds, crosslinked alkoxy silanes (e.g., as described in U.S. Patent No. 5,213,589), polycarbamates and the like. A binder may be included as well.

B. Manufacture

Precisely Shaped Composites

The preferred method for making a useful abrasive article having precisely shaped abrasive composites is described in U.S. Patent Nos. 5,152,917 and 5,435,816. Manufacture is preferably conducted in a clean room type environment (e.g., a class 100, class 1,000, or class 10,000 clean room) to minimize any contamination in the abrasive article.

Other descriptions of suitable methods can be found in U.S. Patent Nos. 5,437,754; 5,454,844; 5,437,7543; 5,435,816; and 5,304,223.

One preferred method involves:

a) preparing a slurry comprising abrasive particles, binder precursor and optional additives;

b) providing a production tool having a front surface and having a plurality of cavities that extend from the front surface;

c) introducing the slurry into the cavities of the production tool;

d) introducing a backing to the front surface of the production tool such that the slurry wets one major surface of the backing to form an article;

e) at least partially curing or gelling the binder precursor before the article departs from the outer surface of the production tool;

f) removing the resulting abrasive article from the production tool to form an abrasive article having precisely shaped abrasive composites bonded to a backing;

g) optionally further curing the binder precursor.

This process is further illustrated in Figure 15. Referring to Figure 15, backing 341 leaves an unwind station 342, and at the same time the production tool (pattern tool) 346 leaves an unwind station 345. Production tool 346 is coated with slurry by means of coating station 344.

the nip roll be made from a structural material such as metal, metal alloys, rubber or ceramics. The hardness of the nip roll can vary anywhere from about 30 to 120 durometer, typically between 60 to 100 durometer and preferably about 90 durometer.

5 Next, some form of energy preferably is transmitted into the slurry to at least partially cure the binder precursor by energy source 348. The selection of the energy source will depend in part upon the chemistry of the binder precursor, production tool and other processing conditions. The energy source should not appreciably degrade the production tool or backing. The term partial cure means
10 that the binder precursor is polymerized to such a state that the slurry does not flow when inverted in the tool. The binder precursor can be fully cured once it is removed from the production tool by any convenient energy source.

 Then, the production tool and abrasive article are separated at angle alpha. The angle alpha is an angle effective to separate the production tool and abrasive
15 article. If the binder precursor is not fully cured, the binder precursor can then be fully cured by either time and/or exposure to an energy source. Next, the production tool is rewound on mandrel 349 so that the production tool can be reused again. Additionally, abrasive article 340 is wound on mandrel 349.

 In another variation of this first method, the slurry can be coated onto the
20 backing and not into the cavities of the production tool. The slurry coated backing is then brought into contact with the production tool such that the slurry flows into the cavities of the production tool. The remaining steps to make the abrasive article are the same as detailed above.

 The energy source can be a source of thermal energy or radiation energy,
25 such as electron beam, ultraviolet light, or visible light. The amount of energy required is dependent upon the chemical nature of the reactive groups in the binder precursor, as well as upon the thickness and density of the binder precursor coating. For thermal energy, an oven temperature of from about 50°C to about 250°C and a duration of from about 15 minutes to about 16 hours is generally sufficient.
30 Electron beam radiation, which is also known as ionizing radiation, can be used at an energy level of about 0.1 to about 10 Mrad, preferably at an energy level of

composites/square centimeter. The cavities can be present in a dot-like pattern where adjacent cavities butt up against one another at their portions where the indentations merge into a common planar major surface of the production tool formed in the interstices of the cavities. Preferably, the shape of the cavities is selected such that the surface area of the abrasive composite decreases away from the backing.

The production tool can be in the form of a belt, a sheet, a continuous sheet or web, a coating roll such as a rotogravure roll, a sleeve mounted on a coating roll, or die. The production tool can be composed of metal, (e.g., nickel), metal alloys, or plastic. The production tool can be fabricated by any conventional technique, including photolithography, knurling, engraving, hobbing, electroforming, diamond turning, and the like. For example, a copper tool can be diamond turned and then a nickel metal tool can be electroplated off of the copper tool. Additional details on how to make a master tool or a production tool can be found in U.S. Patent Nos. 5,152,917; 5,489,235; 5,454,844; 5,435,816; PCT WO 95/07797 and PCT WO 95/22436. In some instances, a photolithography process is desired because it creates patterns that cannot or are otherwise difficult and expensive to generate by other techniques such as diamond turning.

A thermoplastic tool can be replicated off a metal master tool. The master tool will have the inverse pattern desired for the production tool. The master tool is preferably made out of metal, e.g., a nickel-plated metal such as aluminum, copper or bronze. A thermoplastic sheet material optionally can be heated along with the master tool such that the thermoplastic material is embossed with the master tool pattern by pressing the two together. The thermoplastic material can also be extruded or cast onto to the master tool and then pressed. The thermoplastic material is cooled to a nonflowable state and then separated from the master tool to produce a production tool.

Additional information on thermoplastic production tools can be found in U.S. Patent No. 5,435,816. Examples of thermoplastic materials that may be useful to form the production tool include: polyesters, polypropylene, polyethylene, polyamides, polyurethanes, polycarbonates, combinations thereof and the like.

Next, the backing is brought into contact with the slurry and the production tool 355 by a nip roll 356 such that the slurry fills the cavities of the production tool. Then, the slurry-coated backing is removed from the production tool. Upon removal the slurry will have a pattern associated with it; the pattern of abrasive
5 composites is formed from the cavities in the production tool.

Following removal, the slurry-coated backing is exposed to an energy source 357b to initiate the polymerization of the binder precursor and thus forming the abrasive composites; suitable energy sources are the same as those described above for the manufacture of precisely shaped abrasive composites. After curing,
10 the resulting abrasive article is wound onto a roll at station 358. It is generally preferred that the time between release of the slurry-coated backing from the production tool to curing of the binder precursor is relatively minimal (e.g., on the order of seconds to hours). If this time is too long, the slurry will flow and the pattern will distort to such a degree that the pattern essentially disappears.
15 Additional details on how to make this type of abrasive article can be found in U.S. Patent Nos. 4,773,920 and 5,014,468. Optionally, the slurry can be partially cured while in contact with the production tool by energy source 357a, provided that the slurry is removed from the production tool before the binder precursor is cured or solidified sufficiently for it to substantially retain its shape upon removal from the
20 production tool. Subsequent to this, the binder precursor is cured or solidified at energy source 357b.

In a variation of this method, the slurry can be coated onto the backing. The backing is then brought into contact with the production tool such that the cavities of the production tool are filled by the slurry. The remaining steps to make the
25 abrasive article are the same as detailed above. After the abrasive article is made, it can be flexed and/or humidified prior to converting.

In another method of making irregularly shaped composites, the slurry can be coated onto the surface of a rotogravure roll. The backing comes into contact with the rotogravure roll and the slurry wets the backing. The rotogravure roll then
30 imparts a pattern or texture into the slurry. Next, the slurry/backing combination is removed from the rotogravure roll. Next, the resulting construction is exposed to

example of an abrasive coating applied over an embossed backing can be found in U.S. Patent No. 5,015,266.

Another method of making an abrasive article using an embossed backing is described in U.S. Patent No. 5,219,462. A slurry is coated into the recesses of an embossed backing. The slurry contains abrasive particles, binder precursor and an expanding agent. The resulting construction is exposed to conditions such that the expanding agent cause the slurry to expand above the front surface of the backing. Next the binder precursor is solidified to form a binder and the slurry is converted into abrasive composites. The resulting abrasive articles are illustrated in Figures 8 and 9.

Referring to Figure 8, abrasive article 100 comprises embossed backing 102 having recesses 110 with side walls 112 and bottom wall 114. Backing 102 has back surface 106. Abrasive composites 120 are elongate and there are openings 104 between adjacent abrasive composites where the backing is exposed. Abrasive composites 120 comprises abrasive particles 124 and binder 122.

Referring to Figure 9, abrasive article 130 comprises embossed backing 132 having recesses 140 with side walls 142 and bottom wall 144. Backing 132 has back surface 136. Abrasive composites 150 are discrete and there are openings 134 between adjacent abrasive composites where the backing is exposed. Abrasive composites 150 comprises abrasive particles 154 and binder 152. The outer surface of the abrasive composites has rough surface or texture 156 associated with it.

A variation of the embossed backing technique uses a perforated backing having an abrasive coating bonded to the front surface of the backing. This perforated backing will have a series or a predetermined placement of holes or cavities that extend through the width of the backing. The slurry is coated (e.g., knife coated) over the backing. These cavities will inherently create a textured abrasive coating.

Thermoplastic Binders

An alternative method of making the abrasive article is use a thermoplastic binder. The article can be prepared with or without a backing. Typically, the

Designation	Material
CA3	An isopropyl triisostearoyl titanate coupling agent commercially available from Kenrich Petrochemicals Inc., Bayonne, NJ under the trade designation "KR-TTS"
CA4	Octyltriethoxysilane commercially available from DeGussa Corp., Ridgefield Park, NJ
SISOL1	A silica sol having an average particle size of about 20 nanometers, about 34% solids in deionized water, commercially available from Nalco Chemical Co., Napierville, IL under the trade designation "Nalco 1042"
SISOL2	A silica sol having an average particle size of about 60 nanometers, about 50% solids in deionized water and commercially available from Nalco Chemical Co., under the trade designation "Nalco 1060"
HEA	2-Hydroxy ethyl acrylate commercially available from Rohm and Haas Co., Philadelphia, PA under the trade designation "Rocryl 420"
HEMA	Hydroxy ethyl methacrylate commercially available from Rohm and Haas Co., under the trade designation "Rocryl 400"
BP1	An ethoxylated trimethylolpropane triacrylate resin commercially available from Sartomer Co., Inc., Exton, PA under the trade designation "Sartomer 9035"
BP2	A triacrylate of tris(hydroxy ethyl) isocyanurate resin commercially available from Sartomer Co., Inc., under the trade designation "Sartomer 368"
TMPTA	Trimethylolpropane triacrylate commercially available from Sartomer Co., Inc., under the trade designation "Sartomer 351"
HDDA	Hexanediol diacrylate commercially available from Sartomer Co., Inc., under the trade designation "Sartomer 238"
BP3	A polyethylene glycol diacrylate commercially available from Sartomer Co., Inc., under the trade designation "Sartomer 344"
BP4	A one to one mass blend of BP1 and BP2
EPR	A bisphenol A based epoxy resin commercially available from Shell Chemical Co., Houston, TX under the trade designation "EPON 828"
EC	An amine curative commercially available from Air Products Inc., Allentown, PA under the trade designation "Ancamine 1922"
PEG	Polyethylene glycol having an average molecular weight of about 600, commercially available from Union Carbide, Danbury, CT under the trade designation "Carbowax 600"
DPP	Dibutyl phthalate plasticizer commercially available from Eastman Kodak Co., Rochester, NY under the trade designation "Kodaflex DBP"

Designation	Material
PH1	2,4,6-Trimethylbenzoyl-diphenyl-phosphine oxide photoinitiator commercially available from BASF, Charlotte, NC under the trade designation "Lucirin TPO".
PH2	2-benzyl-2-N,N-dimethylamino-1-(4-morpholino-phenyl)-1-butanone, commercially available from Ciba Geigy Corp, Greensboro, NC under the trade designation "Irgacure 369"
PH3	2-isopropylthioxanthone commercially available from Biddle-Sawyer Corp., New York, NY (Distributor for Octel Chemicals, United Kingdom) under the trade designation "Quanticure ITX"
PH4	Ethyl-4-(dimethylamino) benzoate photoinitiator commercially available from Biddle-Sawyer Corp. under the trade designation "EPD"
PH5	2-hydroxy 3(3,4-dimethyl-9-oxo 9H-thioxanthen-2-yloxy)-N,N,N trimethyl-1-propanaminium chloride commercially available from Biddle-Sawyer Corp. under the trade designation "Quanticure QTX"
PH6	2-propoxythioxanthone commercially available from Biddle-Sawyer Corp. under the trade designation "Quanticure PTX"
PH7	2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide liquid photoinitiator commercially available from BASF, Charlotte, NC under the trade designation "Lucirin LR 8893"
CACO	Calcium carbonate filler having an average particle size of about one micrometer, commercially available from Pfizer Specialty Minerals, New York, NY under the trade designation "Superflex 200"
CACO2	Calcium carbonate filler having an average particle size of about 2.6 micrometers, commercially available from Pfizer Specialty Minerals, under the trade designation "USP-MEDIUM"
CACO3	Calcium carbonate filler having an average particle size of about 4.6 micrometers, commercially available from Pfizer Specialty Minerals, under the trade designation "USP-EX-HEAVY"
CACO4	Calcium carbonate filler having an average particle size of about 0.07 micrometer, commercially available from Pfizer Specialty Minerals, under the trade designation "MULTIFLEX-MM"
SA1	A silica suspending agent having a surface area of 50 meters square/gram, commercially available from DeGussa Corp. under the trade name "OX-50"
PLFP	Filler particles having an average particle size between 5 to 7 micrometers, these filler particles were a combination of micronized polyethylene and TEFLON (PTFE) and were commercially available from Micro Powders, Inc. Tarrytown, NY under the trade designation "Polysilk 600"

Designation	Material
SAA	Salicylic acid commercially available from Sigma Chemical Co.
CMS	Calcium metasilicate filler commercially available from Alfa Johnson Matthey under the trade designation "Wollastonite"
ZR	A sintered monoclinic zirconia abrasive particle having an average particle size of about 0.7 micrometer commercially available from Magnesium Electron Inc., Flemington, NJ under the trade designation "SC15"

Preparation of the CEO2 Abrasive Particles

The ceria abrasive particles were treated with a coupling agent in the following manner to form CEO2. The ceria abrasive particles were mixed together with an isopropyl triisostearoyl titanate coupling agent and methyl ethyl ketone solvent. After mixing, a vacuum was applied to remove the organic solvent. Then the ceria particles were dried at room temperature for 48 hours. The resulting abrasive particles contained approximately 1% by weight coupling agent on their surface.

General Procedure I for Making an Abrasive Slurry Comprising a Ceramer Binder and Abrasive Particles

The ceramer binder precursor was first prepared and to this were added additional materials to form the abrasive slurry. To prepare the ceramer binder precursor, the SISOL1 was first charged into a round bottom flask, followed by HEA, CA1 and CA2. This order of addition was important to achieve a uniform ceramer binder precursor and prevent gellation of the ceramer. These materials were mixed together to form a uniform dispersion. Then the flask containing these materials was placed on a rotary evaporator and heated for about 15 minutes at 55°C and continuously stirred. Then a vacuum pump system operating at about 2.64 - 6.60 KPa (20 to 50 mm Hg) was installed to remove a portion of the water while maintaining the rotary evaporator temperature at about 55°C. These conditions were maintained until enough water was removed so that the resulting ceramer was about 66% by weight solids, in about 30 minutes, thus producing the ceramer binder precursor. BPI was then added to the ceramer and the resulting

Then a vacuum pump system operating at about 2.64 - 6.6 KPa (20 to 50 mm Hg) was installed to remove a portion of the water. The rotary evaporator temperature was maintained at about 55°C. The flask containing the materials was subjected to these conditions until enough water was removed so that the resulting ceramer was about 66% solids, in about 30 minutes, thus forming the ceramer binder. Next, 100.0 grams of this ceramer binder precursor were placed into another flask, then 3.65 grams of BP1 and 3.65 grams of BP2 were added to the ceramer and the resulting blend was mixed about one minute. Following this, about 135.0 grams of CEO2 were gradually added and the resulting blend was mixed about four minutes. Following this, 0.5 grams of PH1 were added and the resulting blend was mixed for about two minutes. Following this, 1.2 grams of PH2 were added and the resulting blend was mixed about three to four minutes to form the abrasive slurry.

General Procedure IV for Making an Abrasive Slurry Comprising a Ceramer Binder and Abrasive Particles

The ceramer binder precursor was first prepared and to this were added the additional materials to form the abrasive slurry. To prepare the ceramer binder, 366.4 grams of SISOL1 were first charged into a round bottom flask, followed by 306 grams of CA1 and 71.2 grams of HEA. These materials were mixed together to form a uniform dispersion. Then the flask containing these materials was placed on a rotary evaporator and heated for about 15 minutes at 55°C and stirred continuously. Then a vacuum pump system operated at about 2.6 to 6.6 KPa (20 to 50 mm Hg) was installed to remove a portion of the water. The rotary evaporator temperature was maintained at about 55°C. The flask containing the materials was subjected to these conditions until enough water was removed so that the resulting ceramer was about 66% solids, in about 30 minutes, thus forming the ceramer binder. Next, 40.2 grams of this ceramer binder precursor were placed into another flask, then 0.47 gram of PH2, 0.47 gram of PH5 and 0.47 gram of PH4 were added to the ceramer and the resulting blend was mixed using an air stirrer until the blend was essentially homogeneous. Following this, about 9.8 grams of BP1 and 9.8 grams of BP2 were added and the resulting blend was mixed until the blend was

from 3M, St. Paul, MN, under the trade designation "Scotch Adhesive 7963MP". Then, a 30.5 cm (12 inch) diameter circular test sample was die cut for testing.

General Procedure II for Making the Abrasive Article

5 The abrasive article was made on a machine similar to that illustrated in Figure 15 of the present application. This process was carried out in a class 10,000 clean room. A polypropylene production tool was provided that comprised a series of cavities with specified dimensions arranged in a predetermined order or array. The production tool was essentially the inverse of the desired shape, dimensions and
10 arrangement of the abrasive composites. The production tool was unwound from a winder. The abrasive slurry was coated at room temperature and applied into the cavities of the production tool using a vacuum slot die coater. Next, the PPF backing was brought into contact with the abrasive slurry coated production tool such that the abrasive slurry wetted the front surface of the backing. Afterwards,
15 ultraviolet light radiation was transmitted through the production tool and into the abrasive slurry. Two different ultraviolet lamps were used in series. The first UV lamp was a Fusion System ultraviolet light that used a "V" bulb and operated at 236.2 Watts/cm (600 Watts/inch). The second was an ATEK ultraviolet lamp that used a medium pressure mercury bulb and operated at 157.5 Watts/cm (400
20 Watts/inch). Upon exposure to the ultraviolet light, the binder precursor was converted into a binder and the abrasive slurry was converted into an abrasive composite. Then, the production tool was removed from the abrasive composite/backing and the production tool was rewound. Following this, the abrasive composite/backing, which formed the abrasive article, was wound upon a
25 core. This process was a continuous process that operated at between about 4.6 to 7.6 meters/minute (15 to 25 feet/minute). The abrasive article was then heated for about two minutes at 110 to 115.5°C (230 to 240°F) to activate the primer on the PPF backing.

30 To prepare the abrasive article for testing, the abrasive article was laminated to a pressure sensitive adhesive tape commercially available from 3M, St. Paul, MN, under

radiation passed through the film backing. The speed was about 10.2 meters/minute (35 feet/minute) and the sample was passed through two times.

To prepare the abrasive article for testing, the abrasive article was laminated to a pressure sensitive adhesive tape commercially available from 3M, St. Paul, MN, under the trade designation "Scotch Tape 467MP Hi Performance Adhesive". Then, a 30.5 cm (12 inch) diameter circular test sample was die cut for testing.

General Procedure VI for Making the Abrasive Article

General Procedure VI was essentially the same method as General Procedure V except that the binder precursor was cured by passing the tool together with the backing and binder precursor under one visible light lamp "V" bulb commercially available from Fusion Systems, Inc., that operated at about 600 Watts/inch.

Pattern 1

A production tool was made by casting polypropylene material on a metal master tool having a casting surface comprised of a collection of adjacent truncated pyramids. The resulting production tool contained cavities that were in the shape of truncated pyramids. The pyramidal pattern was such that their adjacent bases were spaced apart from one another no more than about 510 micrometers (0.020 inch). The height of each truncated pyramid was about 80 micrometers, the base was about 178 micrometers per side and the top was about 51 micrometers per side. There were about 50 lines/centimeter delineating the array of composites.

Pattern 2

This arrangement of abrasive composites was similar to Figure 6, each row comprised alternating abrasive composites which had the "cross" shape with abrasive composites which had the "x" shape. In this arrangement, the abrasive composites from the odd rows were offset from the abrasive composites of the even rows. In this arrangement, the total length of both arms of either the cross or the x shape was about 750 micrometers and the width of one arm of either the cross or

surface area so that the effective pressure is less. Because the higher pressure tends to lead to higher cut rates, the high cut rates on the blanket wafers may in fact lead to even higher cut rates on conventional patterned semiconductor wafers.

5 The workpiece, i.e., blanket wafer, was made according to the following procedure. A single crystal silicon base unit having a diameter of 100 mm and a thickness of about 0.5 mm was purchased from Wafernet of San Jose, CA. The silicon base unit was then placed in a furnace having a hydrogen and oxygen atmosphere and the temperature in the furnace increased to 1050°C. A uniform layer of silicon dioxide was thermally deposited over the silicon base, this process
10 being known in the art as a thermal oxide process. The deposited silicon dioxide thickness was between about 7,000 to 20,000 Angstroms, as measured using a measuring device commercially available as machine model #RR/FTM Resist commercially available from Rudolph of Fairfield, NJ. The silicon dioxide thickness was measured five times at each of the following locations: the center, 24 mm
15 directly below the center, 36 mm directly below the center, 24 mm directly above the center and 36 mm directly above the center.

The test machine was a modified Strausbaugh Lapping Machine, Model 6Y-1 similar to the apparatus depicted in Figure 3. The workpiece was assembled into a retaining ring, commercially available from Rodel of Newark, DE. A
20 pressure sensitive adhesive, "Scotch Brand Adhesive #7963MP" commercially available from 3M, St. Paul, MN, was laminated to the back side of the abrasive article. This pressure sensitive adhesive enabled the abrasive article to be secured to a polyester film disc, 40.6 cm (16 inches) in diameter, between the abrasive sample disc and the first support pad. This polyester film prevented the fluid medium from
25 penetrating into the support pads. The first support pad was a polyurethane pad was commercially available from Rodel of Newark, DE under the trade designation "IC1000". The second support pad was a polyurethane impregnated polyester non-woven pad commercially available from Rodel of Newark, DE under the trade designation "SUBA IV". A second support pad was then attached below the first
30 support pad onto the platen of the lapping machine. Each support pad had a diameter of about 30.5 cm (12 inches).

Test Procedure II

Test Procedure II was essentially the same as Test Procedure I except that the gauge or line pressure was about 4.2 kg (9.3lbs) and the down load force was 10.4 kg (23 lbs).

5

Test Procedure III

Test Procedure III was essentially the same as Test Procedure II except that the abrasive article was not conditioned with the aluminum ring prior to use.

10 Test Procedure IV

The following simulated the test procedure for modifying the exposed surface of a semiconductor wafer. There were two parts to the test machine. The base unit which held the workpiece was an Ecomet 4 Variable Speed Grinder-Polisher commercially available from Buehler Ltd., Lake Bluff, IL. The base unit held a 23 cm (9 inch) diameter abrasive disc. The abrasive disc was secured to the base unit by means of a pressure sensitive adhesive commercially available from 3M, St. Paul, MN, under the trade designation "Scotch Brand Adhesive 7963MP". The abrasive disc was die cut from a larger disc or sheet for testing. The blanket wafer workpiece was prepared in the same manner as described in Test Procedure I. Prior to treatment, the workpiece thickness was measured using a FTM commercially available for Nanometrics, Sunnyvale, CA under the trade designation "Nanospec AFT". The head unit was an Automet 2 Power Head commercially available from Buehler Ltd. The workpiece was secured to the rotating Automet 2 Power Head plate by a wafer template commercially available from Rodel, Newark, DE. The head unit containing the abrasive disc was brought into contact with the workpiece. Both the head unit and workpiece rotated in a counter motion relative to one another during treatment. The workpiece rotated about 500 rpm. The treatment was carried out wet, with tap water directed to the center of the workpiece. The treatment time ranged from two to 10 minutes, depending upon the particular example. The pressure between the abrasive disc and the workpiece was about 0.31 kg/cm². After the specified time, the workpiece was rinsed and wiped clean

30

Test Procedure IX

Test Procedure IX was essentially the same as Test Procedure III except that the gauge or line pressure was about 91 Pa (13 psi) and the down load force was 17.25 kg (38 lbs). The test length was two minutes.

5

Test Procedure X

Test Procedure X was essentially the same as Test Procedure III except that the support pad was a polyurethane foam pad commercially available from Rodel under the trade designation "IC1000". Additionally there was a 76 micrometer (3 mil) polyester film between the support pad and the abrasive article being tested.

10

Test Procedure XI

Test Procedure XI was essentially the same as Test Procedure X except that the total treatment time was only one minute.

15

Test Procedure XII

Test Procedure XII was essentially the same as Test Procedure XI except that the pH of the KOH solution was closely controlled to 11.5.

20 Test Procedure XIII

Test Procedure XIII was essentially the same as Test Procedure X except that the pH of the KOH solution was closely controlled to 12.5.

Test Procedure XIV

Test Procedure XIV was essentially the same as Test Procedure IX except the gauge or line pressure was about 112 Pa (16 psi) and the down load force was about 22.7 kg (50 lbs).

25

Test Procedure XVIII

Test Procedure XVIII was essentially the same as Test Procedure III except that a loose abrasive slurry was also added to the wafer surface. The abrasive slurry was pumped over each wafer at a rate of 80 mL/minute. This loose abrasive slurry was in addition to the KOH-based fluid medium. The loose abrasive slurry contained approximately 30% by weight amorphous fumed silica in deionized water. This loose abrasive slurry was purchased from Cabot Corp., Tuscola, IL, under the trade designation "SCI", lot #2G69515.

10 Test Procedure XIX

Test Procedure XIX was essentially the same as Test Procedure XVI except that the pH of the KOH was closely controlled to 11.5 and the support pad was a polyurethane foam pad ("IC1000"). Additionally there was a 76 micrometer thick (3 mil) polyester film between the support pad and the abrasive article.

15

Test Procedure XX

Test Procedure XX was essentially the same as Test Procedure XIX except that the test length was two minutes.

20 Test Procedure XXI

Test Procedure XXI was essentially the same as Test Procedure XIX except that the test length was five minutes.

Examples 1 through 10

25 Examples 1 through 10 compare different formulations of an abrasive slurry that utilized a ceramer binder precursor. The abrasive slurry was prepared according to General Procedure I for Making an Abrasive Slurry Comprising a Ceramer Binder and Abrasive Particles. The materials forming the ceramer are listed in Table 2. The materials forming the abrasive slurry can be found in Table 3.

30 The amounts listed in Tables 2 and 3 are in grams of material. The abrasive article for each example was made according to the General Procedure I for Making the

Table 4
Cut Rate

Ex.	Cut Rate #1	Cut Rate #2	Cut Rate #3	Cut Rate #4	Cut Rate #5	Average Cut Rate
1	1220	1170	960	780	870	1,000
2	90	50	130	80		90
3	300	150	200			220
4	60	40	40	40		50
5	60	50	40	60		50
6	620	470	230	390	150	370
7	2140	2230	2150	740	1590	1770
8	1450	120	250	320		540
9	300	150	200			220
10	210	120				170

Examples 1 through 10 illustrated that different cut rates were achieved by altering the formulation of the abrasive slurry.

Examples 11 through 25

This set of examples compared various compositions of the abrasive slurry. The abrasive articles for this set of Examples were tested according to Test Procedure I, Test Procedure II and Test Procedure III and test results are listed in Tables 7, 8 and 9. In this set of examples, there were one to ten abrasive articles tested per example.

Example 11

The abrasive slurry for Example 11 was made according to General Procedure II for Making an Abrasive Slurry Comprising a Ceramer Binder and Abrasive Particles. The abrasive article was made according to the General Procedure I for Making the Abrasive Article using Pattern #1.

Examples 20 through 25 compare different levels of a plasticizer. The abrasive slurry was prepared by mixing, with an air stirrer, TMPTA, HDDA, CA3, PH3, PH4 and PH2. Next, CEO1 was gradually added to this mixture. It took approximately 15 minutes to blend in the CEO1 into this mixture. Following this, CA1 was added and the resulting blend was mixed for an additional five minutes. Next, CACO (when used) was added to this blend and mixed for about 10 minutes to make the abrasive slurry. The amount of the materials for the abrasive slurries is listed in Table 6. The abrasive article for each example was made according to the General Procedure I for Making the Abrasive Article using Pattern #1.

10

Table 6
Abrasive Slurry Formulations for Examples 20 through 25

Material	20	21	22	23	24	25
TMPTA	24	18	12	6	0	0
HDDA	84	78	72	66	60	48
PEG	12	24	36	48	60	72
CA3	10	10	10	10	10	10
PH3	1.5	1.5	1.5	1.5	1.5	1.5
PH4	3	3	3	3	3	3
PH2	3	3	3	3	3	3
CEO	495	495	495	495	495	495
CA1	30	30	30	30	30	30
CACO	45	45	45	0	45	0

Table 9
Test Procedure I

Ex.	Cut Rate #1	Cut Rate #2	Cut Rate #3	Cut Rate #4	Cut Rate #5	Cut Rate #6	Average Cut Rate
23	1370	1790	1770	1770	1700		1680
23	1500	1490	1650				1550
1,1	1320	1050	790				1050
12	830	1020					930
13	830	840					840
19	430						430
16	160						160

5 Examples 11 through 25 illustrated that different cut rates were achieved by altering the formulation of the abrasive slurry.

Examples 26 and 27

10 These examples compared two formulations of an abrasive slurry containing a ceramer binder. The resulting abrasive articles were tested according to Test Procedure I. The test results are listed in Table 10.

Example 26

15 The abrasive slurry for Example 26 was made according to General Procedure II for Making an Abrasive Slurry Comprising a Ceramer Binder and Abrasive Particles. The abrasive article was made according to the General Procedure I for Making the Abrasive Article using Pattern #1.

Example 27

20 The abrasive slurry for Example 27 was made according to General Procedure III for Making an Abrasive Slurry Comprising a Ceramer Binder and Abrasive Particles. The abrasive article was made according to the General Procedure I for Making the Abrasive Article using Pattern #1.

Procedure I for Making the Abrasive Article using Pattern #1. The abrasive article was tested according to Test Procedure IV.

Example 29

5 The abrasive slurry of Example 29 was prepared as follows. Into a container was added: 20 grams of organic solvent (glycol ether solvent commercially available from Olin Chemicals, Stamford, CT under the trade designation "POLYSOLVE TPM"); 15.0 grams of TDP, 3.68 grams of TMPTA and 55 grams of HDDA. The resulting binder precursor was mixed using an
10 stirrer until the blend was essentially homogeneous. Next, 120 grams of CEO1 were gradually added into the blend and mixed until the blend was essentially homogeneous. Following this, 0.8 grams of PH2, 0.8 grams of PH6 and 0.8 grams of PH4 were added into the blend and mixed until the blend was essentially homogeneous. Next, 80 grams of ASP were gradually added into the blend and
15 mixed until the blend was essentially homogeneous to form the abrasive slurry.

 The abrasive article was tested according to Test Procedure IV and had a cut rate of 900 Angstroms/minute over a 10 minute test. This example illustrated that a relatively high cut rate was achieved with the use of a cerium oxide abrasive particles incorporated into the abrasive structure and in the absence of a potassium
20 hydroxide based fluid medium. Additionally, this example illustrated an abrasive slurry that comprised a high boiling solvent and a photocurable binder precursor. Likewise, this example illustrated an abrasive slurry that comprised a plasticizer, coupling agent and filler.

 The abrasive article of Example 29 was also tested according to Test
25 Procedure V. For a two minute test, the abrasive article produced a cut rate of 3750 Angstroms/minute.

Example 30

 The abrasive slurry for Example 30 was prepared in the same manner as the
30 abrasive slurry for Example 28 except that 0.47 grams of PH2 and 0.2 of PH1 were added instead of the PH5 and PH4 photoinitiators.

Test Procedure IV, except that the tap water was replaced with a potassium hydroxide solution that had a pH between 11.5 to 12.5. The flow rate was approximately 30 mL/minute. The cut rate was measured at five minutes and also at 10 minutes. The test results are listed in Table 12; the cut rates were measured in 5 Angstroms/minute.

Table 12
Test Procedure IV

Ex.	Cut Rate after 5 minutes	Cut Rate after 10 minutes
32	776	794
33	200	132

10 This set of Examples illustrated the effect of different patterns on the cutting ability of the abrasive article.

Examples 34 through 44

15 This set of examples compared various percent solids of the ceramer binder precursor. The ceramer binder precursor was first prepared and after the ceramer binder precursor was prepared, the additional materials were added to the ceramer binder precursor to form the abrasive slurry. To prepare the ceramer binder, the SISOL1 was first charged into a round bottom flask, followed by HEA, CA1 and BP4. The amounts of these materials (in grams) are listed in Table 13. This order
20 of addition was important to achieve a uniform ceramer binder precursor and prevent gellation of the ceramer binder precursor. These materials were mixed together to form a uniform dispersion. Then the flask containing these materials was placed on a rotary evaporator and heated for about 15 minutes at 55°C and continuously stirred. A vacuum pump system operating at about 2.64 - 6.6 KPa (20
25 to 50 mm Hg) was installed to remove a portion of the water. The rotary evaporator temperature was still maintained at about 55°C. The flask containing the materials was subjected to these conditions until enough water was removed so

Table 14
Amount of Materials in Abrasive Slurry For Examples 34 through 43

Ex.	Ceramer Binder Pre-cursor	SISOL2	CA4	CEO2	PH2	PH1	BP4	Water	SISOL2
34	38	10	0.875	21	1	0	0	0	0
35	38	10	0.875	16.8	1	0	0	0	0
36	38	18	1.6	14	1	0	0	0	0
37	38	20	1.75	12.0	1.37	0	0	0	0
38	38	12.54	0.55	16.8	1.0	0	0	0	0
39	35.6	12.54	1.1	16.8	0	1.17	0	0	0
40	35.6	12.54	1.1	16.8	0	1.19	2.4	0	0
41	35.6	10.54	0.92	20.16	0	1.19	2.4	1.0	0
42	35.6	8.13	0.71	24.19	0	1.19	2.4	0	2.21
43	35.6	8.13	0.71	24.19	0	1.19	2.4	0	2.21

5 The abrasive articles were made according to General Procedure I for Making the Abrasive Article using Pattern #1, and were tested according to Test Procedures VI and the test results are listed in Table 15. The cut rates were calculated as Angstroms/minute.

Table 15
Using one workpiece for a total time of 15 to 20 minutes

Example	Cut Rate (Avg.)
34	943.6
35	1000.1
36	1223
37	1478.7
38	437.3
39	13.2
40	80
41	27
42	37
43	942.3

Table 16

Abrasive Slurry Formulations for Examples 44 through 46

Material	Example 44	Example 45	Example 46
TMPTA	11.25	9.38	7.50
HDDA	33.75	28.13	22.50
ABP	30.0	37.50	45.0
CA3	4.95	4.95	4.95
PHI	3.6	3.0	2.4
CEO1	123.75	123.75	123.75
CACO2	68.3	68.3	0.0
CACO	0.0	0.0	68.30

The resulting abrasive articles were tested according to Test Procedure VII.

- 5 The test results are listed in Table 17. Note the cut rate was an average of readings and was measured in Angstroms/minute of material removed.

Table 17

Cut Rate	Example 44	Example 45	Example 46
after 2 minutes of testing*	400	1010	1960
after 4 minutes of testing*	380	1130	2100
after 2 minutes of testing**	Not Tested	Not Tested	1810
after 4 minutes of testing**	Not Tested	Not Tested	1910
after 6 minutes of testing**	Not Tested	Not Tested	2360

- 10 * In this Test Procedure, the abrasive article was made and tested on the same day.

- ** In this Test Procedure, the abrasive article was made three days before it was tested.

15

The data in Table 17 indicated that there was essentially no difference in the cut rates if the abrasive article was tested the same day it was made or if the

and the production tool and into the abrasive slurry. The quartz plate aided in keeping the production tool flat during curing.

5 The resulting abrasive articles were tested according to Test Procedure VII except for the following changes. The abrasive article of Example 47 was tested for only two minutes. The abrasive article of Example 48 was tested for 26 minutes. The test results are listed in Table 19. Note the cut rate was an average of readings and was measured in Angstroms/minute of material removed.

Table 19

Cut Rate after __ minutes of testing	Example 47	Example 48
2	2690	800
4		800
6		930
8		1360
10		1610
12		1800
14		1900
16		2200
18		2460
20		2530
22		2720
24		2370
26		2750

10

Relative to Example 48, it was concluded from the above data that there was a "break in" time for the abrasive article. It appeared that this "break in" time was about the first four minutes, where the abrasive article produced a lower cut rate. After this break in time, the abrasive article generated a higher cut rate.

15 Although not wishing to be bound by any theory, it is speculated that this break in time may be associated with the time it took to remove any outer film of the binder on the abrasive coating.

Examples 49 and 50

20

This set of examples compared various ways to make and to test the abrasive article. The abrasive slurry was prepared by mixing, with an air stirrer, the

Table 21
Abrasive Slurry Formulations for Examples 51 through 56

Material	Ex. 51	Ex. 52	Ex. 53	Ex. 54	Ex. 55	Ex. 56
TMPTA	13.5	13.5	14.25	12.75	12.75	12.75
HDDA	40.5	40.5	42.75	38.25	38.25	38.25
ABP	6	6	3	9	9	9
CA3	5	5	5	5	5	5
PH3	0.6	0.75	0.75	0.75	0.75	0.75
PH4	1.2	1.5	1.5	1.5	1.5	1.5
PH2	1.2	1.5	1.5	1.5	1.5	1.5
CEO1	247.5	247.5	247.5	247.5	247.5	247.5
CA1	0	15	15	15	15	15
CACO	22.5	22.5	22.5	22.5	22.5	22.5

The abrasive article for each example was made according to the General Procedure I for Making the Abrasive Article except for the following changes. Examples 51 through 54 used Pattern #1. Example 55 used Pattern #2. Example 56 used Pattern #3.

For Example 57, the abrasive article was made according to the following procedure. The ceramer binder precursor was first prepared and after the ceramer binder precursor was prepared, the additional materials were added to the ceramer binder precursor to form the abrasive slurry. To prepare the ceramer binder, 457.5 grams of SISOL1 were first charged into a round bottom flask, followed by 88.75 grams of HEA and 37.5 grams CA1. This order of addition was important to achieve a uniform ceramer binder precursor and prevent gellation of the ceramer binder precursor. These materials were mixed together to form a uniform dispersion. Then the flask containing these materials was placed on a rotary evaporator and heated for about 15 minutes at 55°C and continuously stirred. Then a vacuum pump system operating at about 2.64 - 6.60 KPa (20 to 50 mm Hg) was installed to remove a portion of the water. The rotary evaporator temperature was still maintained at about 55°C. The abrasive slurry was prepared by mixing, using

Table 23
Abrasive Slurry Formulations for Examples 58 through 64

Material	Ex. 58	Ex. 59	Ex. 60	Ex. 61	Examples 62, 63 and 64
TMPTA	7.5	12.0	7.5	12	7.5
HDDA	22.50	0	22.50	72	22.5
PEG	0	0	0	36	0
ABP	45.00	12	45.00	0	45.0
CA3	4.95	5	4.95	10	4.95
PH1	2.40	0	2.40	0	2.40
PH3	0	0.75	0	1.5	0
PH4	0	1.5	0	3	0
PH2	0	1.5	0	3	0
CEO1	123.75	247.5	123.75	495	123.75
HEMA	0	15	0	0	0
CA1	0	0	0	30	0
CACO	68.30	22.5	0.0	45	0
CACO2	0.0	0.0	68.30	0	68.30

The abrasive article for Example 58 was made according to the General
 5 Procedure I for Making the Abrasive Article using Pattern # 1. The abrasive article
 for Example 59 was made according to General Procedure III for Making the
 Abrasive Article using Pattern #1. The abrasive articles for Examples 60 through
 64 were made according to General Procedure II for Making the Abrasive Article
 using Pattern #1 except for the following changes. In Example 62, the abrasive
 10 article was not heated. In Example 64, the abrasive article was conditioned for 20
 seconds with the aluminum ring as described above in Test Procedure I.

The resulting abrasive articles were tested according to Test Procedure VII.
 The test results are listed in Table 24. Note the cut rate was an average of five
 readings and was measured in Angstroms/minute of material removed.

The abrasive article for Example 65 was made according to the General Procedure I for Making the Abrasive Article using Pattern # 1 except for the following changes. A glass plate was installed over the production tool and the ultraviolet light was transmitted through the glass plate and through the production tool and into the abrasive slurry.

The abrasive article for Example 66 was made according to the General Procedure I for Making the Abrasive Article using Pattern # 1 except for the following changes. The ultraviolet light was transmitted through the production tool and into the abrasive slurry. Also there was only one pass of the sample under the ultraviolet light.

The abrasive articles for Examples 67 through 70 were made according to the General Procedure I for Making the Abrasive Article using Pattern #1.

The abrasive articles for Examples 65 through 70 were tested according to Test Procedure IX except for the changes noted below. The test results are listed in Table 26. Note the cut rate was an average of five readings and was measured in Angstroms/minute of material removed.

Table 26

Example	Cut Rate	Cut Rate*	Cut Rate**
65	2702		
66	983		
67	1640		
68	2283	2285	2640
69	2318		
70	1240		

* In this test procedure the workpiece rotated at about 60 rpm and the abrasive article rotated at about 70 rpm.

** In this test procedure the workpiece rotated at about 45 rpm and the abrasive article rotated at about 100 rpm.

Table 27

Cut Rate	Example 71	Example 72
after 2 minutes of testing	1260	500
after 4 minutes of testing	1700	1300
after 6 minutes of testing	2080	1750
after 8 minutes of testing	2310	1990
after 10 minutes of testing		2260
after 12 minutes of testing		2120
after 14 minutes of testing		2530

Examples 73 and 74

An abrasive slurry for Example 73 was prepared by mixing, with an air stirrer, 7.5 grams of TMPTA, 22.50 grams of HDDA, 45.0 grams of DUP, 4.95 grams of CA3 and 2.40 grams of PHI. Next, 123.75 grams of CEO1 were gradually added. It took about 15 minutes to blend in the CEO1. Following this, 110. grams of CACO3, 20.0 grams of CACO2 and 10.0 grams of CACO4 were gradually added and the resulting blend was mixed for an additional five minutes.

An abrasive slurry for Example 74 was prepared by mixing, with an air stirrer, 7.5 grams of TMPTA, 22.50 grams of HDDA, 45.0 grams of PP, 4.95 grams of CA3 and 2.40 grams of PHI. Next, 123.75 grams of CEO1 were gradually added. It took about 15 minutes to blend in the CEO1. Following this, 200.0 grams of CACO3 were gradually added and the resulting blend was mixed for an additional five minutes.

The abrasive articles for Examples 73 and 74 were made according to the General Procedure I for Making the Abrasive Article using Pattern #1 except for the following changes. A rubber roller was not used. Additionally, there was a quartz plate over the production tool and the ultraviolet light was transmitted through the quartz plate and the polymeric tooling. The abrasive articles for Examples 73 and 74 were tested according to Test Procedure VII. The test results

To prepare the abrasive article for testing, two abrasive articles were joined together and laminated to a pressure sensitive adhesive tape commercially available from 3M, St. Paul, MN, under the trade designation "Scotch 467MP Hi Performance Adhesive". Then, a 30.5 cm (12 inch) diameter circular test sample was die cut for testing.

The resulting abrasive article was tested according to Test Procedure VII. After two minutes of testing, the cut rate was 1090 Angstroms/minute. After four minutes of testing, the cut rate was 1370 Angstroms/minute.

10 Example 76

The abrasive article of Example 76 was made from an abrasive slurry that used a partially polymerized ethylenically unsaturated monomer made according to the following procedure. First, 209.5 grams of isooctyl acrylic acid and 0.81 grams of bensildimethyl-ketal photoinitiator were added into a vessel. The resulting mixture was first purged with nitrogen for 15 minutes. Then the vessel was exposed to a single Black Lamp that operated at 15 Watts for 30 seconds to partially polymerize the acrylate monomer. The resulting partially polymerized isooctyl acrylic acid had a viscosity of about 7800 centipoise.

An abrasive slurry for Example 76 was prepared by mixing, with an air stirrer, 1.18 parts CA3, 6.54 parts HDDA, 3.08 parts TMPTA, 16.15 parts PP, 1.0 part PH7 and 1.15 parts of the partially polymerized ethylenically unsaturated monomer. Next, 47.57 parts of CEO1 were gradually added. It took about 15 minutes to blend in the CEO1 into this mixture. Following this of 23.33 parts of CaCO3 were gradually added and the resulting blend was mixed for an additional five minutes.

The abrasive article for Example 76 was made according to the General Procedure I for Making the Abrasive Article using Pattern #1 except for the following changes. A rubber roller was not used. Additionally, there was a quartz plate over the production tool and the ultraviolet light was transmitted through the quartz plate and the polymeric tooling. The abrasive article for Example 76 tested according to Test Procedure VII. The test results are listed in Table 29. Note the

Table 30
Abrasive Slurry Formulations for Examples 77 through 80

Material	Ex. 77	Ex. 78	Ex. 79	Ex. 80
TMPTA	8.44	8.44	8.44	8.44
HDDA	25.31	25.31	25.31	25.31
PP	41.25	41.25	41.25	41.25
CA3	4.95	4.95	4.95	4.95
PH7	2.40	2.40	2.40	2.40
CEO1	30.94	61.88	92.81	123.75
CACO3	71.91	68.07	64.25	60.42
CACO2	17.05	13.21	9.39	5.56
CACO4	12.88	9.04	5.22	1.39

5 The abrasive article for each example was made according to General Procedure IV for Making the Abrasive Article using Pattern #1. The resulting abrasive articles were tested according to Test Procedure XI. The test results can be found in Table 31. The cut rate was measured as Angstroms of silicon dioxide removed in the one minute interval.

10

Table 31

Example	Cut Rate Angstroms/minute
77	148
78	500
79	1311
80	1580

This data indicated that there were differences in how much silicon dioxide was removed by the abrasive article depending upon the amount of ceria present.

Examples 85 through 87

This set of examples, prepared as described for Examples 77-80, compared various abrasive slurry formulations that contained different levels of plasticizer to make the abrasive article. The amount of materials is listed in Table 34.

5

Table 34

Abrasive Slurry Formulations for Examples 85 through 87

Material	Ex. 85	Ex. 86	Ex. 87
TMPTA	11.25	9.38	8.44
HDDA	33.75	28.13	25.31
PP	30	37.5	41.25
CA3	4.95	4.95	4.95
PH7	3.6	3.0	2.7
CEO1	123.75	123.75	123.75
CACO3	67.37	67.37	67.37

10 The abrasive article for each example was made according to General Procedure I for Making the Abrasive Article using Pattern #1. The resulting abrasive articles were tested according to Test Procedure X. The test results can be found in Table 35. The cut rate was measured as Angstroms of silicon dioxide removed in the one minute interval.

15

Table 35

Example	Cut Rate Angstroms/minute
85	497
86	1060
87	1382

Table 37
Test Procedures XII and XIII

Example	Test Procedure XII Cut Rate Angstroms/Minute	Test Procedure XIII Cut Rate Angstroms/Minute
88	62	84
89	2113	2045
90	1462	916
91	1546	1220

5 This data indicated that there were differences in how much silicon dioxide was removed by the abrasive article depending upon the materials and their respective amounts present in the abrasive coating. Additionally, this data indicated that there were differences in the cut rate depending upon how the ultraviolet light was transmitted into the abrasive slurry to solidify the binder precursor. Likewise, this data indicated that there were differences in the cut rate depending upon the pH
10 of the KOH solution.

Examples 92 and 93

This set of examples, prepared as described in Examples 77-80, compared two different plasticizers in the abrasive slurry formulations that were used to make
15 the abrasive article. The amount of materials is listed in Table 38.

It should be noted that, after testing, the abrasive article from Example 93 was severely damaged and unusable in the testing of any additional semiconductor wafers. This data indicated that there were differences in how much silicon dioxide was removed according to the plasticizer present in the abrasive coating.

5

Examples 94 and 95

This set of examples, prepared as described in Examples 77-80, compared monofunctional acrylates in the abrasive slurry formulations that were used to make the abrasive article. The amount of materials is listed in Table 40.

10

Table 40
Abrasive Slurry Formulations for Examples 94 and 95

Material	Example 94	Example 95
HDDA	7.16	7.10
MA1	63.91	0
MA2	0	64.50
CA3	0.76	0.74
KD2	0.74	0.75
PH7	2.28	2.27
CE01	184.8	184.6
CAC03	75.84	59.9
CAC02	5.59	16.28
CAC04	1.4	1.40

The abrasive articles for these examples were made according to the General Procedure VI for Making the Abrasive Article using Pattern #1. The resulting abrasive article was tested according to Test Procedure XIV. The test results are detailed in Table 41. Note the cut rates were averages of one to ten readings and were measured in Angstroms/minute of material removed.

20

Table 41

Example	Cut Rate Angstroms/Minute
94	1140
95	2240

Examples 99 through 102

This set of examples demonstrated the use of an air corona post-treatment as means to dress the fixed abrasive article. The abrasive slurry was prepared by mixing, with an air stirrer, TMPTA, HDDA, PP, CA3, and PH7. Next, CEO1 was gradually added to the mixture. Following this, calcium carbonate was gradually added. The amount of the materials, in grams, for the abrasive slurry is listed in Table 44.

Table 44
Abrasive Slurry Formulations for Examples 99 through 102

Material	Abrasive Slurry Formulations for Examples 99 through 102
TMPTA	540
HDDA	1620
PP	3240
CA3	356.4
PH7	172.8
CEO1	8910
CACO3	5760
CACO5	176
CACO2	400
CACO4	100

The fixed abrasive articles for these examples were made according to the General Procedure II for Making the Abrasive Article using Pattern #1. The abrasive articles of Examples 99 through 101 were treated with an air corona using a Sherman corona treating unit (Sherman Treaters, Ltd., United Kingdom) in the bare ground role configuration. The abrasive article of Example 99 was treated with the air corona at an energy level 31.2 joules/cm². The abrasive article of Example 100 was treated with the air corona at an energy level 41.2 joules/cm². The abrasive article of Example 101 was treated with the air corona at an energy level 50 joules/cm². Additionally the abrasive articles of Examples 100 and 101 were treated twice at half the energy density to obtain the total energy level. The abrasive article of Example 102 was not air corona treated. This set of abrasive articles was tested according to Test Procedure XIV. Note the cut rate is an

Table 46
Abrasive Slurry Formulations for Examples 103 through 108

Material	Ex. 103	Ex. 104	Ex. 105	Ex. 106	Ex. 107	Ex. 108
TMPTA	9.38	9.38	9.38	9.54	9.54	9.54
HDDA	28.13	28.13	28.13	28.61	28.61	28.13
PP	37.50	37.50	37.50	36.85	36.85	37.5
CA3	4.95	4.95	4.95	4.95	4.95	4.95
PHI	3.00	3.00	3.00	2.4	2.4	3.00
CEO1	123.75	123.75	123.75	120	120	120
SIZR	56.0	0	0	0	0	0
SIN	0	75	0	0	0	0
YZR1	0	0	120	0	0	80
ZR	0	0	0	125	0	0
YZR2	0	0	0	0	125	45

The abrasive articles for Examples 103 through 108 were made according to
5 General Procedure IV for Making the Abrasive Article using Pattern #1. The
resulting abrasive articles were tested according to Test Procedure XV. The test
results can be found in Table 47. The cut rate was measured as Angstroms/minute
of silicon dioxide removed. The test length varied.

clean air. The surface finish of the wafer was measured using a Wyko Interferometer, Model # RST Plus, Tucson, AZ. The surface finish was measured in five different locations. The test results can be found in Table 48.

5

Table 48
Surface Finish Measurements of the 21st Test Wafer by Example 108

Location	RMS*	Ra
1	0.79 nm	0.62 nm
2	0.93 nm	0.75 nm
3	0.95 nm	0.75 nm
4	0.95 nm	0.76 nm
5	0.77 nm	0.62 nm

*RMS refers to the root mean square of the deviation from the reference plane.

10

Example 109

The abrasive slurry for this example contained an ammonium salt. The abrasive slurry was prepared by mixing, with an air stirrer, TMPTA, HDDA, CA3 and PH1. Next, CEO1 was gradually added to the abrasive slurry until it was substantially dispersed. Following this, the other abrasive particles and NHC were also gradually mixed into the abrasive slurry until they were substantially dispersed. The amount of materials is listed in Table 49.

15

Table 49
Abrasive Slurry Formulation for Example 109

Material	Ex. 109
TMPTA	18.75
HDDA	56.25
CA3	4.95
PH1	3.00
CEO1	80
ZR	147.2
NHC	10.4

20

Table 51
Abrasive Slurry Formulations for Examples 110 and 111

Material	Example 110	Example 111
TMPTA	11.25	14.26
HDDA	33.75	42.77
PP	30	0
CA3	4.95	0
KD2	0	3.04
PH1	3	1.82
YZR1	87.47	0
ZRO	83.05	0
YZR2	0	221.68
TANA	20	0
SAA	0	20

The abrasive articles for Example 110 and 111 were made according to General Procedure IV for Making the Abrasive Article using Pattern #1. The resulting abrasive articles were tested according to Test Procedures XVI. The test results can be found in Table 52. The cut rate was measured as Angstroms/minute of silicon dioxide removed. The test length was variable and the cut rate was measured after a single minute of treatment.

10

Table 52

Cut Rate (Angstroms/ minute)	Example 110	Example 111
after 1 minute of testing	200	1270
after 2 minutes of testing	150	340
after 3 minutes of testing		230

It can be seen from the above data that different cut rates were achieved with abrasive articles that were made with different abrasive slurries.

Table 54

Example	TIR Prior to Treatment	TIR After Treatment
112	600 nm	210 nm
113	600 nm	183 nm
114	600 nm	72 nm

This data indicated that different abrasive coating formulations achieved different TIR levels.

5

Examples 115 through 117

This set of examples compared various abrasive slurry formulations that were used to make the abrasive article. The abrasive slurry was prepared by mixing, with an air stirrer, HDDA, MA2, CA3 and PH7. Next, CEO1 was gradually added to the abrasive slurry until it was substantially dispersed. Following this, CACO3, CACO2 and CACO4 were also gradually mixed into the abrasive slurry until these particles were substantially dispersed. The amount of materials, in grams, for the abrasive slurries can be found in Table 55.

10

15

Table 55

Abrasive Slurry Formulations for Examples 115 through 117

Material	Example 115	Example 116	Example 117
HDDA	7.50	9.00	10.51
MA2	67.53	66.0	64.50
CA3	4.95	4.97	4.95
PH7	2.40	2.42	2.42
CEO1	123.78	123.78	123.75
CACO3	84.03	84.01	83.05
CACO2	5.62	5.61	5.62
CACO4	1.41	1.41	1.40

Table 57
Abrasive Slurry Formulations for Examples 118 through 122

Material	Ex. 118	Ex. 119	Ex. 120	Ex. 121	Ex. 122
TMPTA	8.47	8.46	8.46	8.44	8.44
HDDA	25.35	25.34	25.53	25.34	25.31
PP	41.29	41.3	41.27	41.28	41.25
CA3	4.96	4.98	4.96	4.96	4.95
PH7	2.40	2.44	2.41	2.42	2.42
CEO1	123.77	0	0	0	0
CEO3	0	123.80	0	0	0
CEO4	0	0	0	123.76	0
CEO5	0	0	123.76	0	0
CEO6	0	0	0	0	123.75
CACO3	60.41	60.41	60.43	60.41	60.40
CACO2	5.64	3.62	5.63	5.61	5.60
CACO4	1.42	1.43	1.40	1.41	1.40

- The abrasive articles for Examples 118 through 122 were made according to
- 5 General Procedure VI for Making the Abrasive Article using Pattern #1. The resulting abrasive articles were tested according to Test Procedure XIX. The test results can be found in Table 58.

Table 58

Example	Average Cut (Angstroms/ minute)
118	1846
119	1651
120	859
121	1368
122	490

The amount of materials, in grams, for the abrasive slurries can be found in Table 60.

Table 60
Abrasive Slurry Formulations for Examples 125 through 129

Material	Ex. 125	Ex. 126	Ex. 127	Ex. 128	Ex. 129
MA3	8.44	11.25	16.85	18.75	15.0
HDDA	25.32	33.75	50.55	56.25	45.0
PP	41.25	30.0	7.50	0	15.0
CA3	4.95	4.95	4.95	4.95	4.95
PH7	2.70	2.70	2.70	6.0	2.70
CEO1	123.75	123.75	123.75	123.75	123.75
CACO3	67.36	67.36	67.36	67.36	67.36
CACO4	8.0	8.0	13.0	15.0	13.0

The abrasive articles for Examples 125 through 129 were made according to General Procedure IV for Making the Abrasive Article using Pattern #1. The resulting abrasive articles were tested according to Test Procedure XII. The test results can be found in Table 61.

Table 61

Example	Average Cut (Angstroms/ minute)
125	1996
126	1107.5
127	320.0
128	146.7
129	420.0

It was evident from the above data that there were differences in cut rate depending upon the formulation of the abrasive slurry.

It was evident from the above data that there were differences in cut rate depending upon the formulation of the abrasive slurry.

Examples 132 through 134

- 5 This set of examples, prepared by the procedure described in Examples 77-80, compared various abrasive slurry formulations that were used to make the abrasive articles. The amount of materials is listed in Table 64.

10

Table 64
Abrasive Slurry Formulations for Examples 132 through 134

Material	Ex. 132	Ex. 133	Ex. 134
MA2	18.75	3.68	3.68
HDDA	56.25	11.03	11.03
CA3	4.95	0.97	1.41
PH7	6.0	1.18	1.18
CEO1	123.75	24.26	35.26
CACO3	67.36	13.20	13.20
CACO4	8	3.57	0

15

The abrasive article for Examples 132 through 134 were made according to General Procedure IV for Making the Abrasive Article using Pattern #1. The resulting abrasive articles were tested according to Test Procedure XII. The test results are in Table 65.

Table 65

Example	Average Cut (Angstroms/ minute)
132	583.3
133	516.7
134	340.0

this data that the addition of a small amount of a dispersing agent can lower the viscosity of the resulting abrasive slurry.

Example 137

5 This example used a zircon opacified glass frit as the abrasive particle. The abrasive slurry was prepared by mixing, with an air stirrer, 3.75 grams of TMPTA, 11.25 grams of HDDA, 22.51 grams of PP, 0.96 gram of CA3 and 1.21 grams of PH7. Next, 47.50 grams of a zircon opacified glass frit was gradually added to the abrasive slurry until it was substantially dispersed. Following this, 20.02 grams of
10 CACO3, 2.02 grams of CACO2 and 2.01 grams CACO4 were gradually mixed into the abrasive slurry until these particles were substantially dispersed. The zirconia opacified glass frit had an average particle size of 3.67 micrometers and contained 25 to 50% by weight silica, about 14% zirconia, 14% of a mixture of alumina, boron oxide and calcium oxide. This particle was commercially available from
15 Ferro Corporation, Cleveland, Ohio under the trade designation "CZ-110". The abrasive article for Example 137 was made according to General Procedure VI for Making the Abrasive Article using Pattern #1. The resulting abrasive article was tested according to Test Procedure XII. After 33 seconds the wafer slipped from the retaining ring. The cut rate was extrapolated to 360 Angstroms/minute.

20

Examples 138 and 139

This set of examples compared various processes for making the abrasive article and the cut performance of the resulting abrasive articles. The same abrasive slurry was used in both examples. The abrasive slurries were prepared by mixing,
25 with an air stirrer, 8.44 parts TMPTA, 25.31 parts HDDA, 41.25 parts PP, 4.95 parts CA3 and 2.40 parts PH7. Next, 123.75 parts of cerium oxide abrasive particles (CEO1) were gradually added to the abrasive slurry until it was substantially dispersed. Following this, 60.40 parts of CACO3, 5.60 parts of CACO2 and 1.40 parts of CACO4 were also gradually mixed into the abrasive
30 slurry until these particles were substantially dispersed.

CACO₃, 5.56 parts of CACO₂ and 1.39 parts of CACO₄ were also gradually mixed into the abrasive slurry until these particles were substantially dispersed into the abrasive slurry. The abrasive article for Example 142 was made according to General Procedure V for Making the Abrasive Article Using Pattern #1.

- 5 The resulting abrasive article was tested according to Test Procedure XIX, except that the pH level was varied. The test results can be found in Table 68.

Table 68
Different pH Levels

pH	Cut Rate (Angstroms/minute)
7 deionized water only	1433
8.5	1530
9.5	1248
10.5	1550
11.5	1366
12.5	1316

10

Examples 141 through 144

This set of examples, prepared as described in Examples 77-80, compared various abrasive slurry formulations that were used to make the abrasive articles. The amount of materials is listed in Table 69.

15

Example 145

This example demonstrated the effect of different retaining ring materials on the amount of silicon dioxide removed by the abrasive article. An abrasive slurry was prepared by mixing, with an air stirrer, 320.63 parts TMPTA, 961.88 parts HDDA, 1567.50 parts PP, 188.10 parts CA3 and 91.20 parts PH1. Next, 4702.50 parts of CEO1 were gradually added to the abrasive slurry until it was substantially dispersed into the abrasive slurry. Following this, 2296 parts of CACO3, 211 parts of CACO2 and 52.8 parts of CACO4 were also gradually mixed into the abrasive slurry until these particles were substantially dispersed into the abrasive slurry. The abrasive article for Example 145 was made according to General Procedure II for Making the Abrasive Article Using Pattern #1, except the ultraviolet light radiation was transmitted through the film backing.

The retaining ring was an annular ring, 10.2 cm (4 inch) inner diameter, 12.7 cm (5 inch) outer diameter, 0.95 cm (0.375 inch) thick, and was fabricated from various phenolic composite materials, as described below.

The material for the retaining rings was commercially available from Minnesota Plastics of Eden Prairie, MN.

The abrasive article was tested according to Test Procedure XIV, substituting the different retaining rings for the Rodel retaining ring. The gauge or line pressure for the LE test holder was about 280 Pa (40 psi). The test results are in Table 71.

Retaining ring XXX was made from a paper/phenolic composite.

Retaining ring LE was made from a cotton cloth/phenolic composite.

Retaining ring NI was made from a nylon cloth/phenolic composite.

Table 71
Test Procedure I ; Different Retaining Rings

Test Holder	Cut Rate (Angstroms/minute)
XXX	390
LE	380
NI	1410

Claims

1. A method of modifying an exposed surface of a semiconductor wafer comprising the steps of:

5 (a) contacting said surface with a three-dimensional, textured, fixed abrasive article comprising a plurality of abrasive particles and a binder arranged in the form of a pre-determined pattern; and

(b) relatively moving said wafer and said fixed abrasive article to modify said surface of said wafer.

10

2. A method according to claim 1 comprising contacting said surface with said fixed abrasive article in the presence of a liquid.

3. A method according to claim 2 comprising contacting said surface
15 with said fixed abrasive article in the presence of a liquid having a pH of at least about 5.

4. A method according to claim 1 wherein said exposed surface comprises silicon dioxide.

20

5. A method according to claim 1 comprising modifying the exposed surface of a processed semiconductor wafer.

6. A method according to claim 1 comprising relatively moving said
25 wafer and said fixed abrasive article to modify said surface of said wafer to create a surface having an Ra value of no greater than about 20 Angstroms.

7. A method according to claim 1 comprising relatively moving said
wafer and said fixed abrasive article to achieve an average cut rate of at least about
30 500 Angstroms/minute to modify said surface of said wafer.

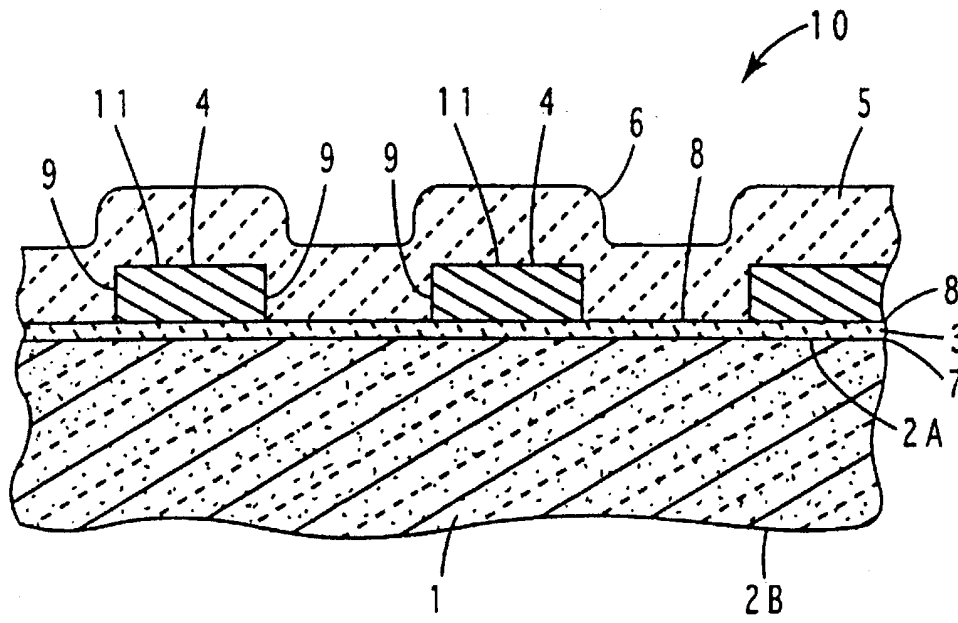


FIG. 1

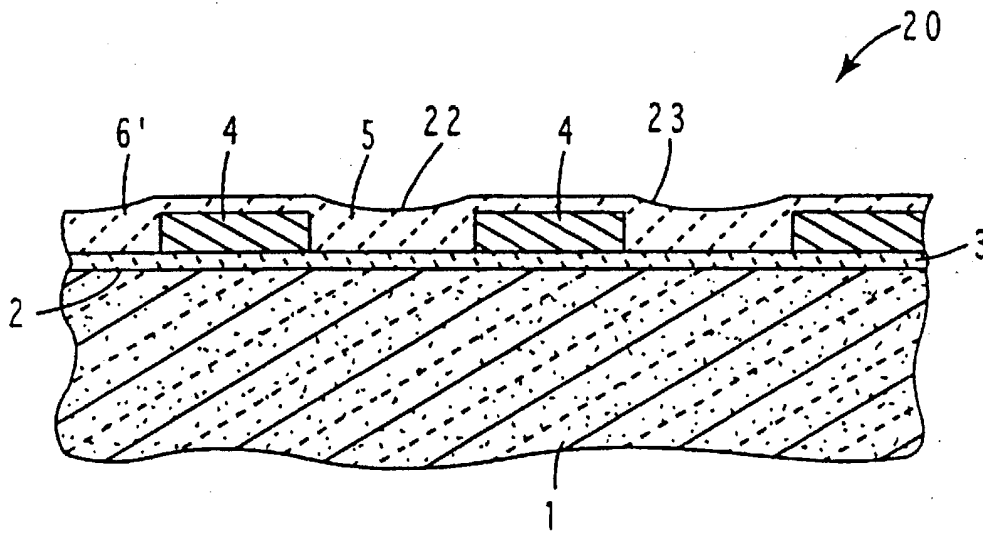


FIG. 2

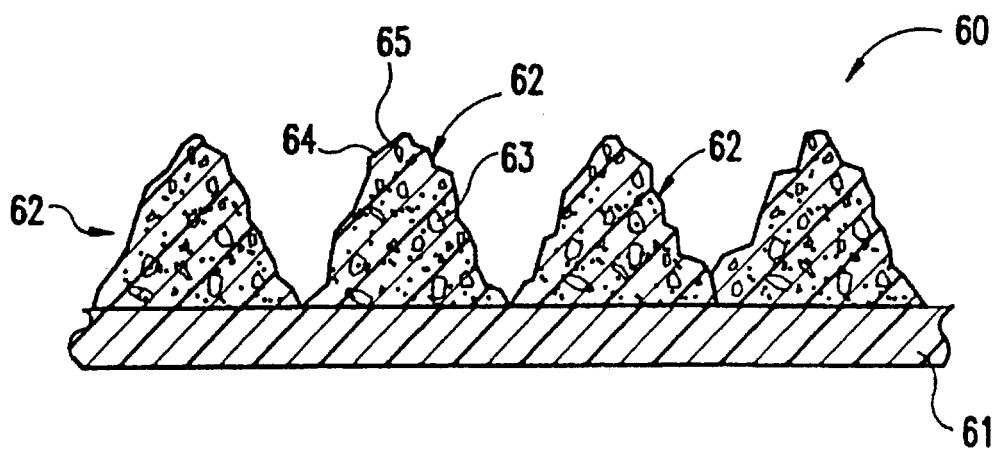


FIG. 5

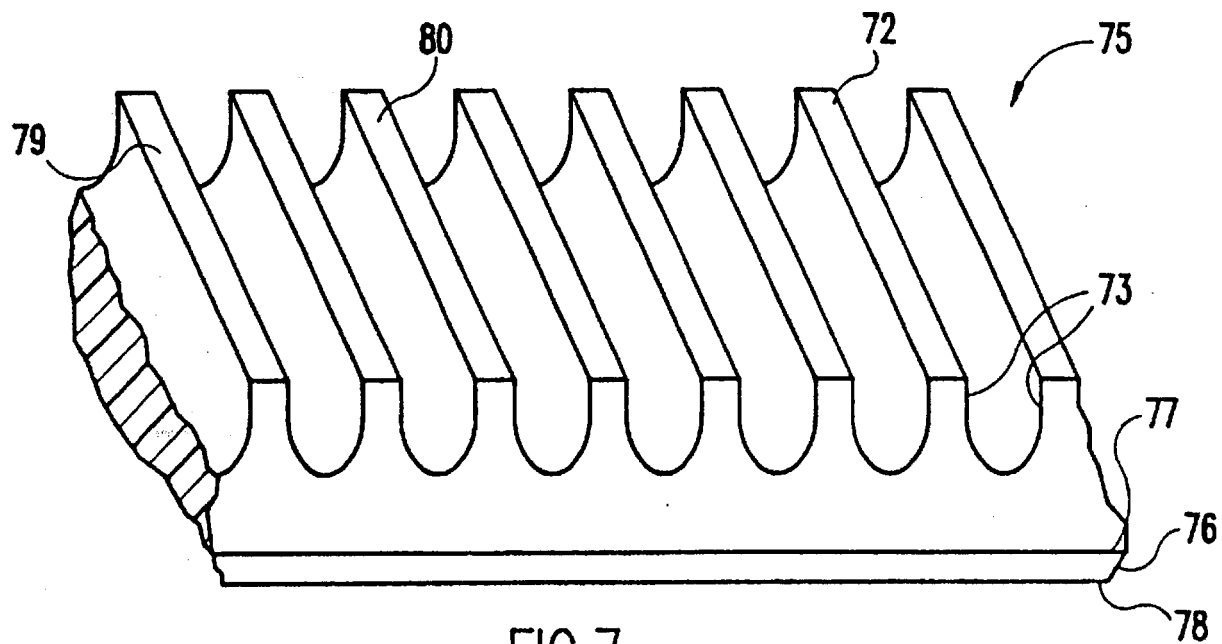


FIG. 7

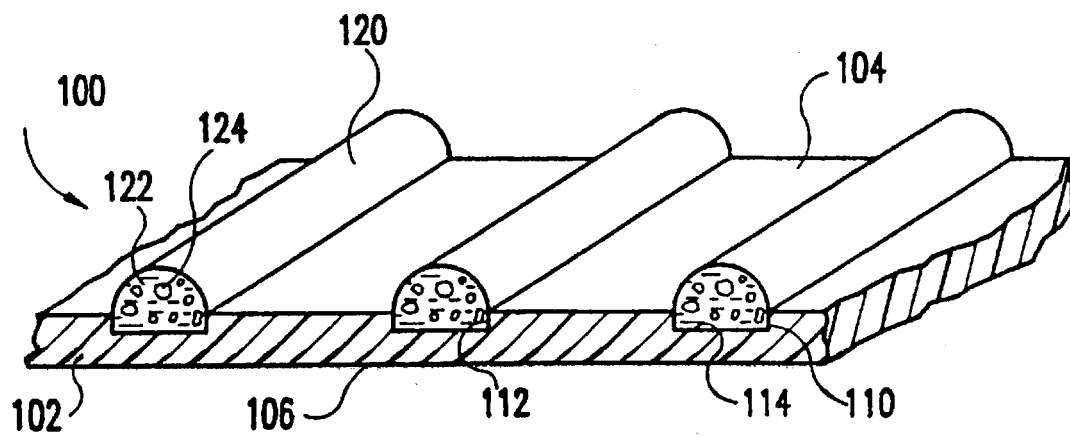


FIG. 8

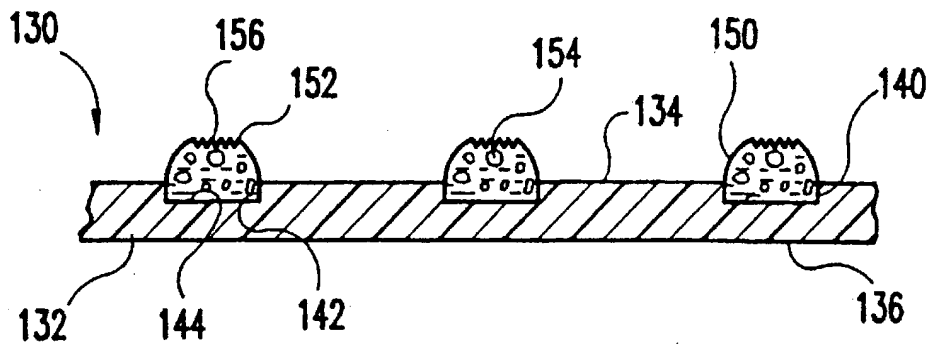


FIG. 9

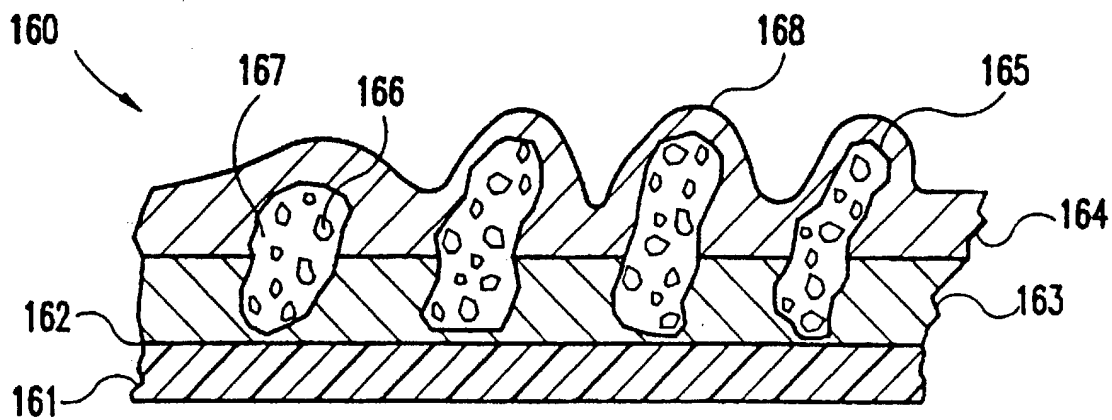


FIG. 10

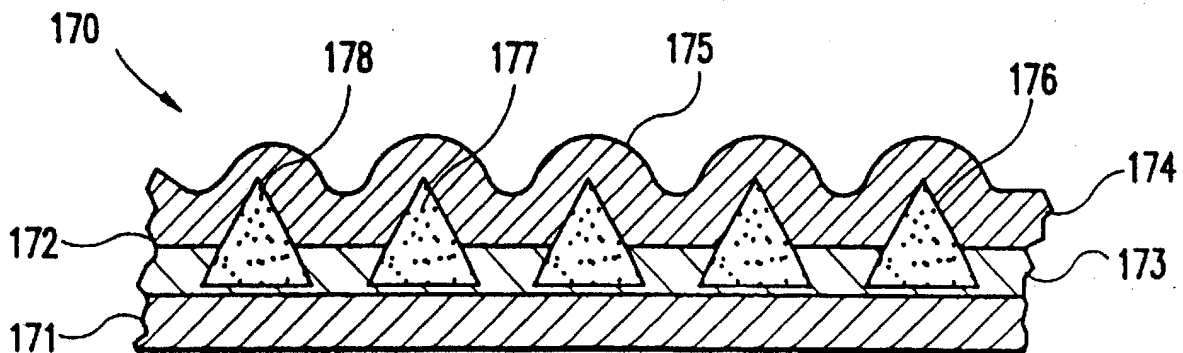


FIG. 11

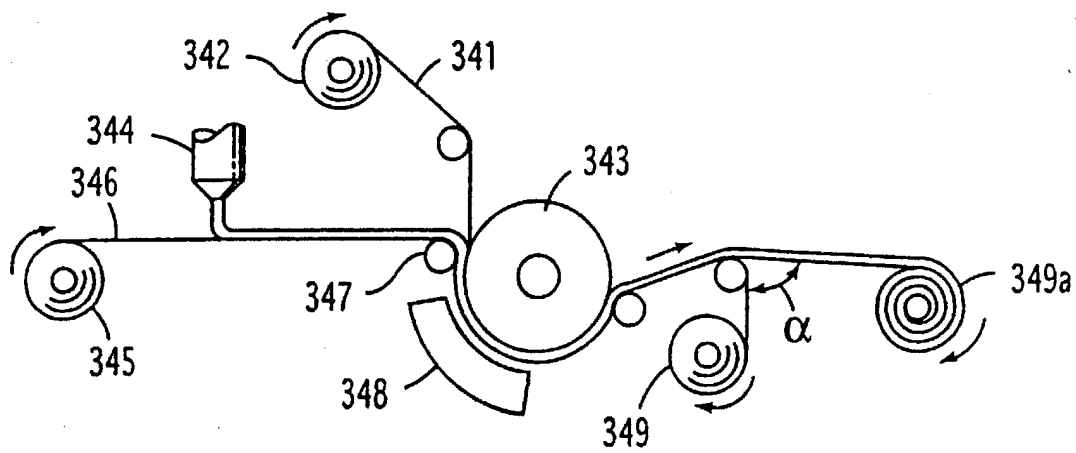


FIG. 15

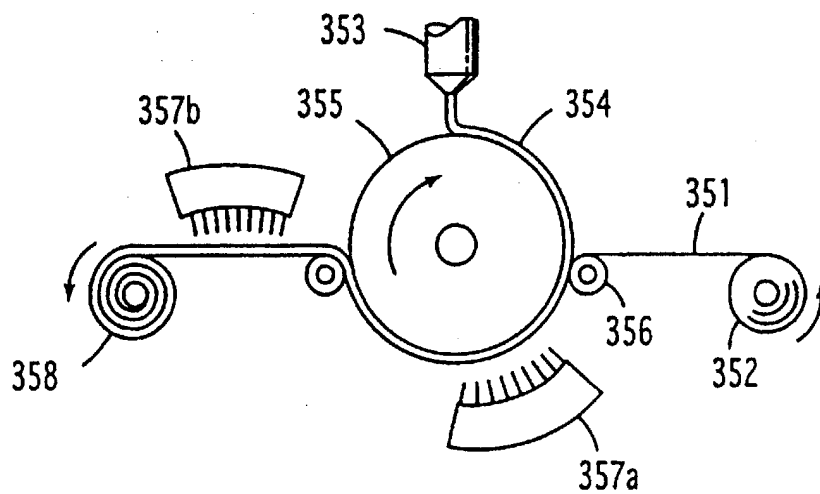


FIG. 16

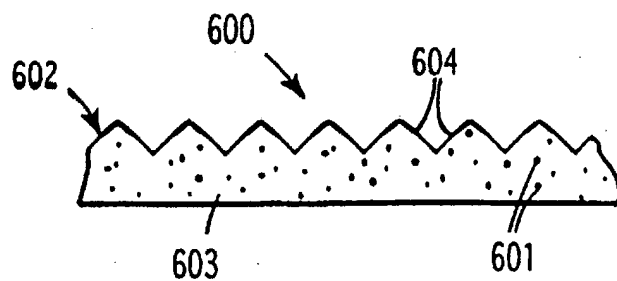


FIG. 17

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 447 885 (FUJIMI ABRASIVE) 25 September 1991 see page 2, line 2 - line 7 see page 2, line 35 - line 40 see page 2, line 57 - page 3, line 2; figure 1 see page 3, column 10 - column 16 ---	1,2
A	US,A,5 152 917 (PIEPER JON R ET AL) 6 October 1992 see claims 1,3-7 ---	1,2,9, 14,15
A,P	US,A,5 500 273 (HOLMES GARY L ET AL) 19 March 1996 see claims 1-5 -----	15